

## Electronic Supplementary Information For:

### Actinide Tetra-N-Heterocyclic Carbene ‘Sandwiches’

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## General Considerations for Synthesis:

All reactions, workups and manipulations involving the NHC metal complexes and subsequent reactions were done using standard Schlenk techniques under N<sub>2</sub> or in an MBraun Unilab glovebox under N<sub>2</sub> unless otherwise stated. All glassware for aforementioned reactions were dried at 170 °C overnight before use. For air sensitive reactions, tetrahydrofuran (THF), toluene, and hexanes were dried on an Innovative Technologies Pure Solv MD-7 Solvent Purification System, degassed by three freeze-pump-thaw cycles on a Schlenk line, and subsequently stored over activated 4 Å molecular sieves prior to use. Anhydrous acetonitrile (CH<sub>3</sub>CN) was prepared by distillation over phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>), followed by degassing by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves prior to use. Benzene pentane, 1,4-dioxane and 1,2-dimethoxyethane (DME) were purchased anhydrous from Sigma-Aldrich, degassed by three freeze-pump-thaw cycles and subsequently stored over activated 4 Å molecular sieves prior to use. For anhydrous NMR solvents, benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>), methylene chloride-*d*<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>), acetonitrile-*d*<sub>3</sub> (CD<sub>3</sub>CN) and tetrahydrofuran-*d*<sub>8</sub> (THF-*d*<sub>8</sub>) were degassed by three freeze-pump-thaw cycles and subsequently stored over activated 4 Å molecular sieves prior to use. C<sub>2</sub>-functionalized end-capped silica gel (40-63 μm diameter) was either purchased from Silicycle (as Silibond C<sub>2</sub>-Functionalized Irregular Silica Gel) or synthesized from literature procedures.<sup>1, 2</sup> Celite and C<sub>2</sub> silica gel used in the purification of metal complexes were dried overnight at 240 °C and subsequently stored in the glovebox prior to use. U<sub>4</sub>(1,4-dioxane)<sub>2</sub>,<sup>3</sup> ThCl<sub>4</sub>(DME)<sub>2</sub>,<sup>4</sup> [H<sub>4</sub>(<sup>B</sup>Me<sub>2</sub>,MeTC<sup>H</sup>)]Br<sub>2</sub>,<sup>5</sup> [H<sub>4</sub>(<sup>B</sup>Me<sub>2</sub>,EtTC<sup>H</sup>)]Br<sub>2</sub>,<sup>6</sup> diphenyldiazomethane,<sup>7</sup> tolyl azide,<sup>8</sup> and thianthrenium hexafluorophosphate<sup>9</sup> were prepared by previous literature procedures. 1,1'-diacetylferrocenium hexafluorophosphate was prepared based on a previous literature procedure, with the use of nitrosonium hexafluorophosphate [NO][PF<sub>6</sub>] as the oxidant, and the product exhibited identical spectral properties.<sup>10</sup> All other reagents were purchased from commercial vendors at highest purity.

## General Considerations for Characterization:

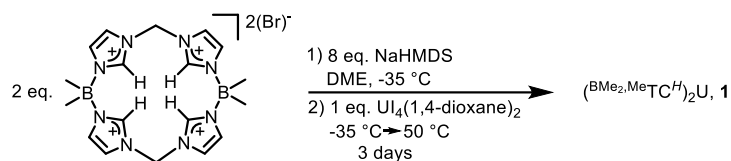
Solution <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR were performed on either a Varian Mercury 300 MHz or Varian VNMRs 500 MHz narrow-bore broadband system at 298 K. All <sup>1</sup>H and <sup>13</sup>C shifts were referenced to the residual solvent. All solution 2D NMR experiments were performed on Varian VNMRs 600 MHz narrow-bore broadband system at 298 K. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance (ATR) using the neat complexes. UV-vis measurements were taken inside a dry glovebox on an Ocean Optics USB4000 UV-vis system with 1 cm path length quartz crystal cell. NIR UV-VIS measurements were collected on a VWR UV-1600 PC spectrophotometer using an air-free, quartz crystal cell with a 1 cm path length. Carbon, hydrogen, and nitrogen analyses were obtained from Midwest Microlab, Indianapolis, IN. Cyclic voltammetry measurements were made inside a dry glovebox at ambient temperature using a BASi Epsilon electrochemical analyzer with a platinum

working electrode, platinum wire counter electrode, and Ag wire reference electrode. For all samples, a 0.1 M solution of tetrabutylammonium hexafluorophosphate ((TBA)(PF<sub>6</sub>)) in the appropriate solvent (such as CH<sub>3</sub>CN) was used as the supporting electrolyte. All peaks were referenced to an external standard of ferrocene. Unless otherwise state, all experiments were conducted by first going to more oxidizing potentials, followed by reduction.

### **General Considerations for Crystallography:**

All X-ray data collections were performed on single crystals coated in Fomblin (**1**) or Paratone oil (**2** and **3**) on glass slides and mounted on nylon fibers. X-ray data for all complexes were collected with the use of a Mo microsource using either an Oxford Diffraction Excalibur Eos CCD (**1**) or a Bruker D8 Venture (**2** and **3**) diffractometer. Crystals were mounted in either a 120 K (**1**) or 100 K (**2** and **3**) cold stream provided by an Oxford Cryostream low-temperature apparatus. All data sets were reduced with Bruker SAINT and were corrected for absorption using either Analytical (**1**) or SADABS (**2** and **3**). Structures were solved and refined using SHELXT and SHELXLE64, respectively. All compounds were treated with PLATON SQUEEZE to remove heavily disordered toluene molecules. In each case (compounds **1-3**), one molecule of toluene was found per complex.

## Synthesis of $(\text{BMe}_2, \text{MeTC}^H)_2\text{U}$ , **1**:



To a 20 mL scintillation vial,  $[\text{H}_4(\text{BMe}_2, \text{MeTC}^H)]\text{Br}_2$  (0.4668 g, 0.8678 mmol, 2 eq.) was added with 15 mL of DME. The vial was cooled to  $-35\text{ }^\circ\text{C}$  in a freezer over 30 mins. To this vial, NaHMDS (0.6365 g, 3.471 mmol, 8 eq.) was added as a solid. The vial was stirred and returned to the freezer to keep cold. This stirring was repeated every minute over 10 minutes. To the resulting brown/yellow solution,  $\text{U}_4(1,4\text{-Dioxane})_2$  (0.4005 g, 0.4339 mmol, 1 eq.) was added in one solid portion, causing the solution to turn an intense dark brown instantaneously. The reaction was then heated at  $50\text{ }^\circ\text{C}$  for 3 days. The solution was filtered over a short pad of Celite and washed with a small amount of DME (5 mL). The solution was concentrated to dryness and triturated with hexanes (3x5 mL) to remove residual DME. The resulting residue was washed 3 times with 1:1 hexanes:toluene solution (20 mL in total), filtered over a small amount of Celite and was chilled at  $-35\text{ }^\circ\text{C}$  overnight, yielding dark purple crystals. The solution was removed and the crystals were washed twice with 5 mL of hexanes and dried, resulting in **1**. Additional complex **1** could be obtained by washing the residue with 1:1  $\text{CH}_2\text{Cl}_2$ :pentane solution (20 mL total), filtration over a small amount of Celite and drying thoroughly, yielding a dark purple powder. The combined crops resulted in 0.0395 g of complex (9.3% yield). Single crystals of **1** were grown by layering hexanes into a solution of **1** in toluene.

An alternative work up purification method of **1** is described below in the preparation of **2**.

**$^1\text{H}$  NMR** ( $\text{CD}_2\text{Cl}_2$ , 599.74 MHz): 14.75 (s, 4H), 8.35 (s, 4H), 7.95 (s, 4H), 4.45 (s, 12H), 1.91 (s, 4H), -8.50 (s, 12H), -12.94 (s, 4H), -55.87 (s, 4H).

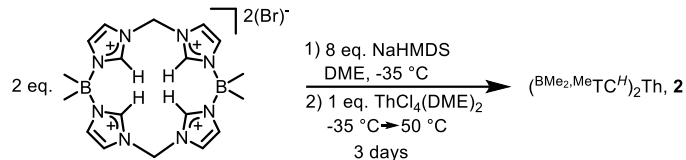
**Solution magnetic moment (Evans NMR method):**  $3.0\ \mu_{\text{B}}$

**IR:** 3132, 2909, 1551, 1494, 1456, 1411, 1333, 1300, 1281, 1260, 1197, 1157, 1137, 1106, 1050, 1034, 1018, 947, 835, 793, 722, 695, 682, 633.

**CHN:** Calculated for  $\text{C}_{36}\text{H}_{48}\text{B}_4\text{N}_{16}\text{U} \cdot \frac{1}{2}\text{C}_7\text{H}_8$ : C: 46.27, H: 5.14, N: 21.56. Found: C: 46.51, H: 5.53, N: 21.08. Toluene confirmed by  $^1\text{H}$  NMR integration (See Figure S2)

**UV-Vis (THF):** 469 nm (250 L/cm $\cdot$ mol), 558 nm (1250 L/cm $\cdot$ mol)

## Synthesis of $(\text{BMe}_2\text{MeTC}^H)_2\text{Th}$ , **2**:



To a 200 mL Schlenk flask,  $[\text{H}_4(\text{BMe}_2\text{MeTC}^H)_2]\text{Br}_2$  (1.421 g, 2.642 mmol, 2 eq.) was added with 60 mL of DME. The flask was cooled to  $-35\text{ }^\circ\text{C}$  in a freezer over the course of 30 mins. To this, NaHMDS (1.910 g, 10.42 mmol, 8 eq.) was added as one portion and the flask was stirred briefly and returned to the freezer to keep cold. The stirring was repeated every minute over 10 minutes. To the solution, which turned a dark brown/yellow color,  $\text{ThCl}_4(\text{DME})_2$  (0.7212 g, 1.302 mmol, 1 eq.) was added as a solid. The Schlenk flask was then sealed, removed from the glovebox and heated in an oil bath at  $50\text{ }^\circ\text{C}$  for 3 days. The solvent was then removed from the reaction and thoroughly dried under high vacuum. The flask was then returned into the glovebox, and suspended in roughly 20 mL of toluene. The brown/red slurry was passed over a  $\text{C}_2$  terminated silica plug (a half-filled 60 mL filtration frit) and washed through with roughly 100 mL of toluene. The resulting colorless solution was concentrated to roughly 5 mL, transferred to a 20 mL vial, and layered with 15 mL of hexanes. The solution was stored at  $-35\text{ }^\circ\text{C}$  for 2 days, resulting colorless crystals of **2**. The solution was decanted off and the residue was washed two times with 5 mL of hexanes, resulting in **2** in very low yield (0.0098 g, 0.7% yield).

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 599.74 MHz): 7.20 (s, 4H), 7.03 (s, 4H), 6.89 (s, 4H), 6.72 (s, 4H), 6.34 (d,  $J = 13\text{ Hz}$ , 4H), 5.30 (d,  $J = 13\text{ Hz}$ , 4H), 0.29 (s, 12H),  $-0.61$  (s, 12H).

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 149.94 MHz): 210.14, 207.64, 123.70, 122.72, 117.94, 116.92, 63.46, 13.35, 11.77.

**IR**: 3134, 2934, 1548, 1458, 1408, 1349, 1300, 1283, 1260, 1194, 1155, 1137, 1104, 1088, 1057, 1035, 1018, 945, 833, 796, 723, 702, 684, 634.  $\text{cm}^{-1}$ .

**CHN**: Calculated for  $\text{C}_{36}\text{H}_{48}\text{B}_4\text{N}_{16}\text{Th} \cdot \frac{1}{2}\text{C}_6\text{H}_{14}$ : C: 45.78, H: 5.42, N: 21.90. Found: C: 45.37, H: 5.58, N: 19.24. Hexanes confirmed by  $^1\text{H}$  NMR integration (See Figure S7).

### Synthesis of $(\text{BMe}_2, \text{EtTC}^H)_2\text{U}$ , **3**:



To a 20 mL scintillation vial,  $[\text{H}_4(\text{BMe}_2, \text{EtTC}^H)]\text{Br}_2$  (0.1228 g, 0.2170 mmol, 2 eq.) was added with 5 mL of DME. The vial was cooled to  $-35\text{ }^\circ\text{C}$  in a freezer over 30 minutes. To this vial, NaHMDS (0.1592 g, 0.8680 mmol, 8 eq.) was added in one solid portion. This solution was stirred and returned to the freezer to keep cold. This was repeated every minute over 10 minutes. To the resulting orange/pink solution,  $\text{U}_4(1,4\text{-dioxane})_2$  (0.1012 g, 0.1085 mmol, 1 eq.) was added in one portion, resulting in an intensely dark brown solution instantaneously. The solution was then heated at  $50\text{ }^\circ\text{C}$  for 3 days. The reaction mixture was concentrated to dryness and dried further by addition and removal of hexanes (3 x 2 mL). To the resulting residue, toluene was added (5 mL) and it was allowed to stir. The solution was then filtered over a short Celite plug and washed through with an additional 5 mL of toluene. The solution was concentrated to roughly 1 mL and stored at  $-35\text{ }^\circ\text{C}$  overnight, resulting in a few orange crystals, which were confirmed by SCXRD to be **3**. Considerable difficulty in purification, scale up, and intrinsic low yield precluded any further characterization of **3**.

### **Reactions to target Installation of a Ninth Ligand to 1:**

Example reaction:

To a 20 mL scintillation vial with a stirbar containing **1** (0.0050g, 0.0057 mmol, 1 eq.) was added a diphenyldiazomethane (0.0017g, 0.0097 mmol, 1.7 eq.) solution in 1 mL of C<sub>7</sub>D<sub>8</sub>.

Experiments with other potential donors included tolyl azide, 4-(trifluoromethyl)-phenylazide, diisopropylcarbodiimide, methyl iodide and diethyl zinc.

In each case, the reaction was stirred at ambient temperature, and then heated to 110 °C if no visible reaction was observed. The reaction was monitored by <sup>1</sup>H NMR spectroscopy.

In all cases, no visible reaction occurred at ambient temperature which showcases the stability of **1**. At elevated temperatures (100-110 °C), by <sup>1</sup>H NMR spectroscopy it was determined that either the reagent or **1** or both decomposed. In the case of methyl iodide, we were able to assign the major decomposition product as 1,1'-methylenediimidazole by <sup>1</sup>H NMR.

### **Reactions to Target the Oxidation of 1 to U(V):**

The following procedure was utilized for a variety of reagents, but one example is shown below:

In a 4 mL shell vial, **1** (0.0050g, 0.0057 mmol, 1 eq.) was added. Separately, thianthrenium hexafluorophosphate (0.0022 g, 0.0057 mmol, 1 eq.) was weighed and was added to the vial with **1** with roughly 0.7 mL of CD<sub>3</sub>CN. The resulting solution was transferred to a J-Young NMR tube and monitored periodically with <sup>1</sup>H NMR (Figures S16-S17).

This procedure was repeated with AgOTf (in THF-d<sub>8</sub>, Figures S12-S13) and 1,1-diacetylferrocenium hexafluorophosphate (in CD<sub>3</sub>CN, Figures S14-S15). In no case were we able to determine a single oxidized U(V) species by <sup>1</sup>H NMR.

**Table S1:** Crystallographic data for compounds **1**, **2** and **3**.

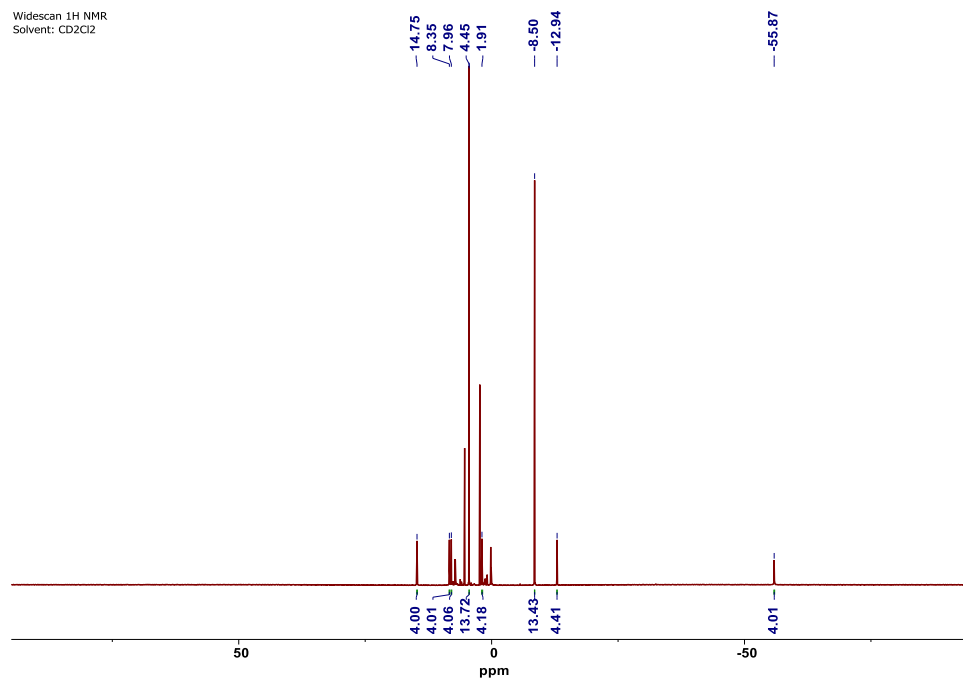
Molecule	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>36</sub> H <sub>48</sub> B <sub>4</sub> N <sub>16</sub> U	C <sub>36</sub> H <sub>48</sub> B <sub>4</sub> N <sub>16</sub> Th	C <sub>40</sub> H <sub>56</sub> B <sub>4</sub> N <sub>16</sub> U
Color	Purple	Colorless	Orange
Formula weight	986.17	980.18	1042.27
Temperature (K)	120(2)	100(2)	100(2)
Source/Wavelength (Å)	Mo/ 0.71073	Mo/0.71073	Mo/ 0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	Fddd
a (Å)	18.5705(2)	18.388(3)	14.113(3)
α (°)	90	90	90
B (Å)	11.30970(10)	11.1669(16)	20.628(4)
β (°)	94.3050(10)	94.007(5).	90
C (Å)	21.6322(3)	22.459(3)	37.423(7)
γ (°)	90	90	90
Volume (Å <sup>3</sup> )	4530.52(9)	4600.4(12)	10895(3)
Z	4	4	8
Density (g/cm <sup>-3</sup> )	1.446	1.415	1.271
μ (mm <sup>-1</sup> )	3.627	3.285	3.021
Independent reflections	10386	90914	4557
R <sub>1</sub> /wR <sub>2</sub>	0.0365/0.0553	0.0206/0.0470	0.0663/0.1219



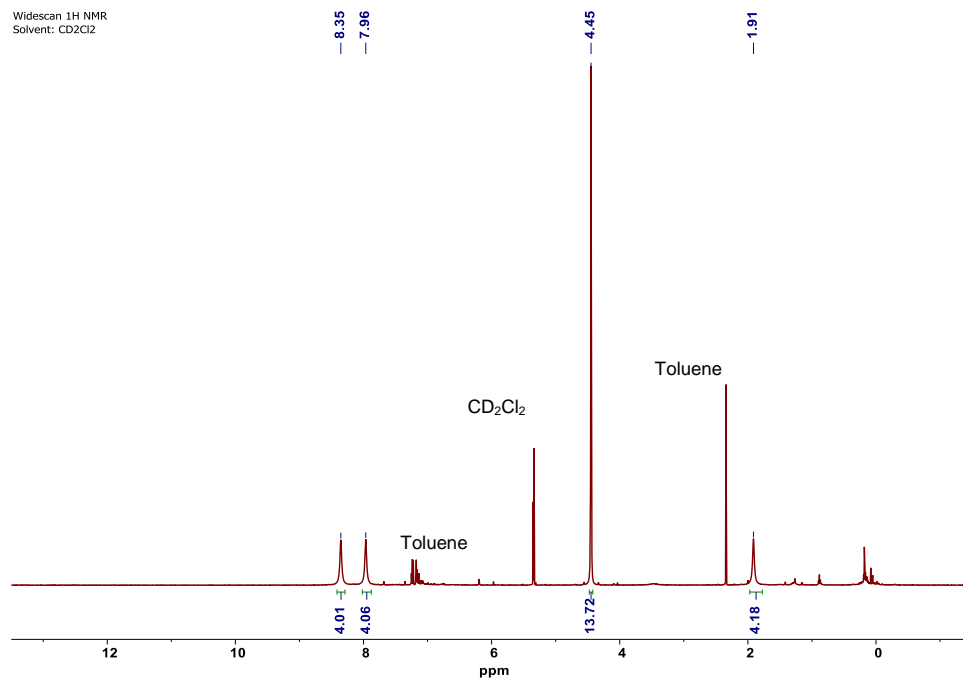
**Table S2:** Selected bond lengths for compounds **1**, **2** and **3**.

Molecule	<b>1</b> (U-C)	<b>2</b> (Th-C)	<b>3</b> (U-C)
M-C <sub>1</sub> (Å)	2.645(3)	2.6926(14)	2.615(4)
M-C <sub>2</sub> (Å)	2.626(3)	2.6987(14)	2.700(4)
M-C <sub>3</sub> (Å)	2.653(3)	2.6974(14)	-
M-C <sub>4</sub> (Å)	2.632(3)	2.6989(14)	-
M-C <sub>5</sub> (Å)	2.621(3)	2.7251(14)	-
M-C <sub>6</sub> (Å)	2.617(3)	2.7045(14)	-
M-C <sub>7</sub> (Å)	2.614(3)	2.7158(15)	-
M-C <sub>8</sub> (Å)	2.620(3)	2.6995(14)	-
M-C Average (Å)	2.629	2.704	2.658

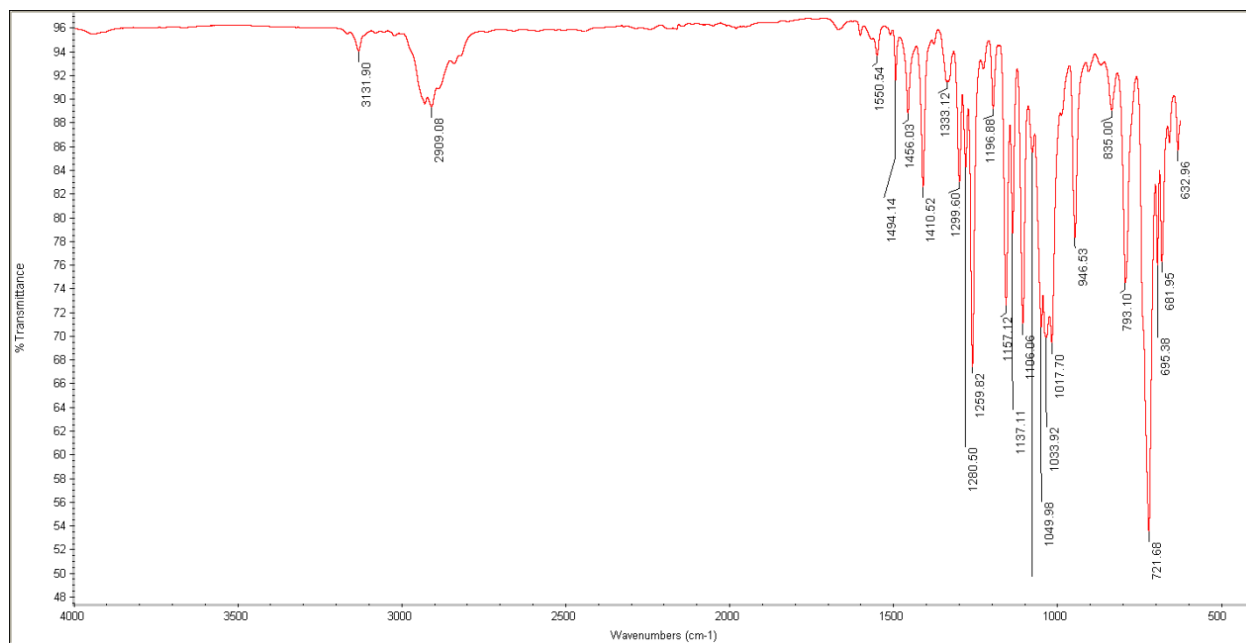
## Selected Annotated Spectra for 1 and 2.



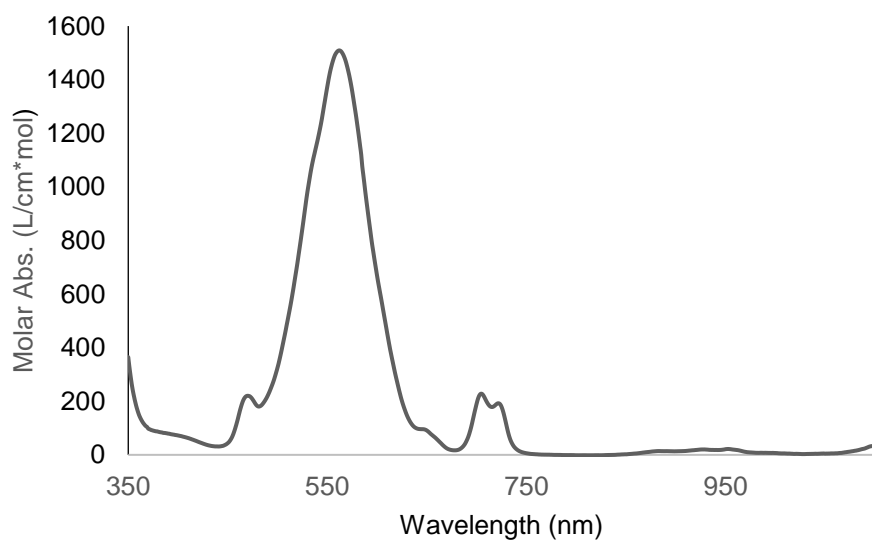
**Figure S1:** Widescan  $^1\text{H}$  NMR of  $(\text{BMe}_2, \text{MeTC}^H)_2\text{U}$  (**1**) in  $\text{CD}_2\text{Cl}_2$ .



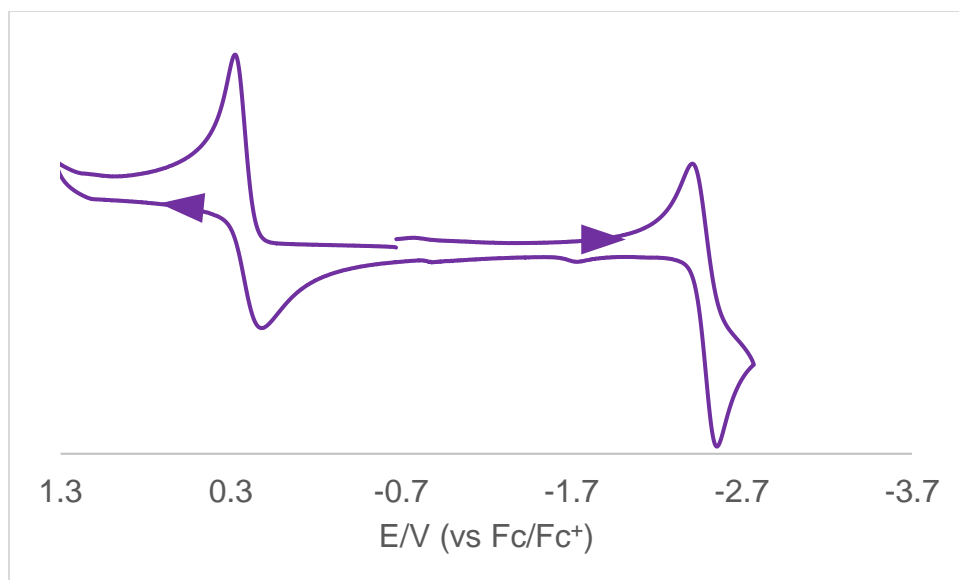
**Figure S2:** Close up of diamagnetic region of the  $^1\text{H}$  NMR of  $(\text{BMe}_2, \text{MeTC}^H)_2\text{U}$  (**1**).



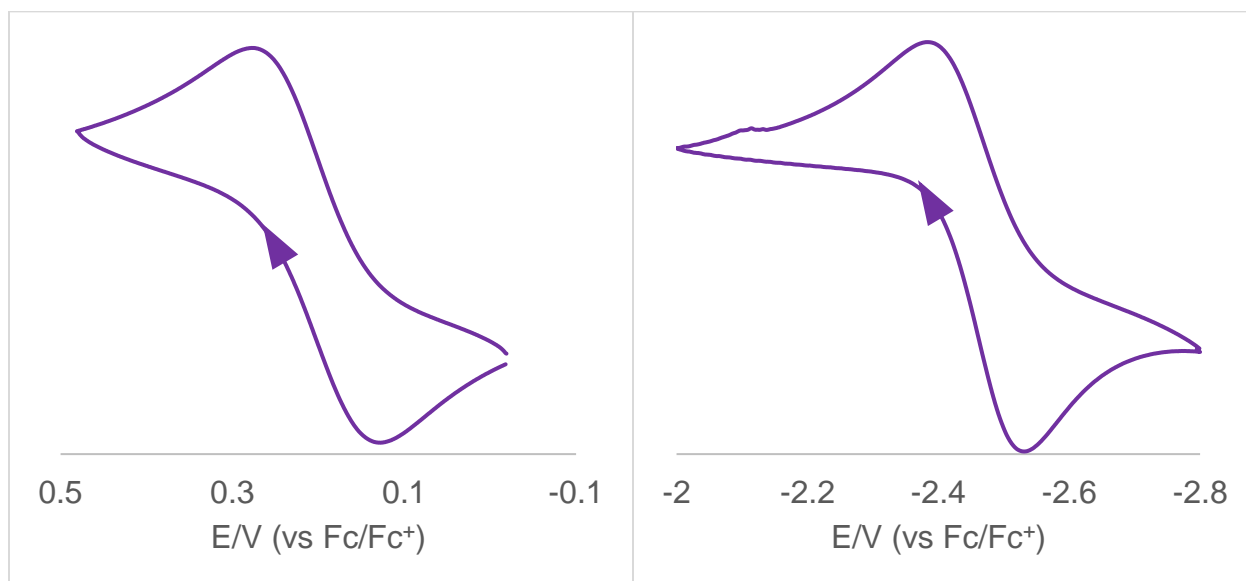
**Figure S3:** ATR IR of neat  $(BMe_2,MeTC^H)_2U$  (**1**).



**Figure S4:** UV-Vis spectrum of  $(BMe_2,MeTC^H)_2U$  (**1**) in  $CH_2Cl_2$ .  $\lambda_{max}$ , ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ): 470 (220), 562 (1500), 704 (230), 722 (190).

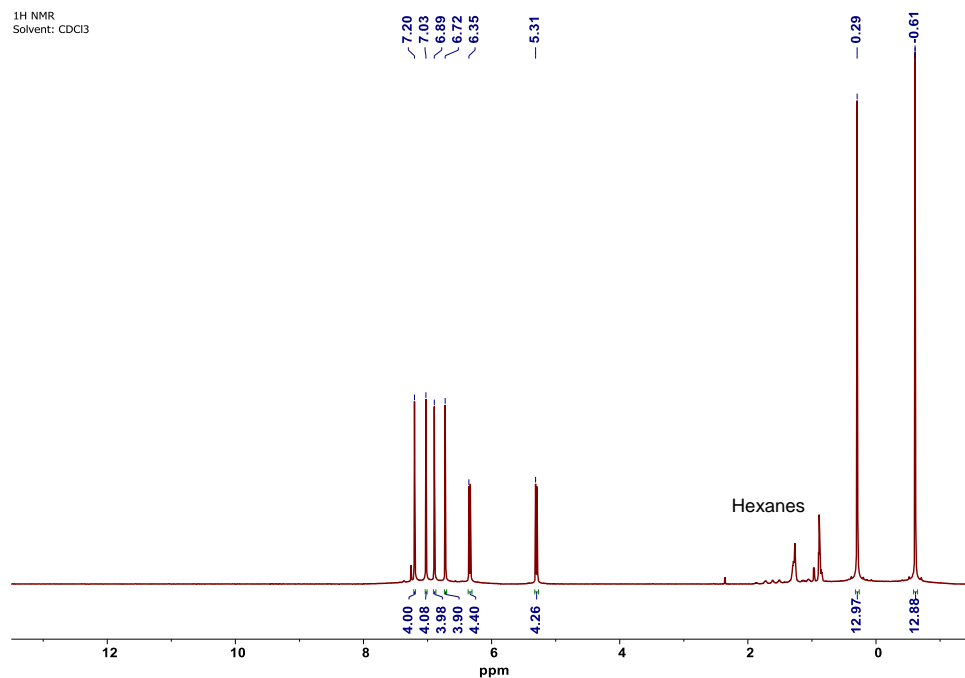


**Figure S5:** Widescan cyclic voltammogram of  $(^{\text{BMe}_2,\text{MeTC}^{\text{H}}})_2\text{U}$  **1** in  $\text{CH}_3\text{CN}$  using 0.1 M  $(\text{TBA})(\text{PF}_6)$  as the supporting electrolyte. Scan rate was run at 100 mV/s.



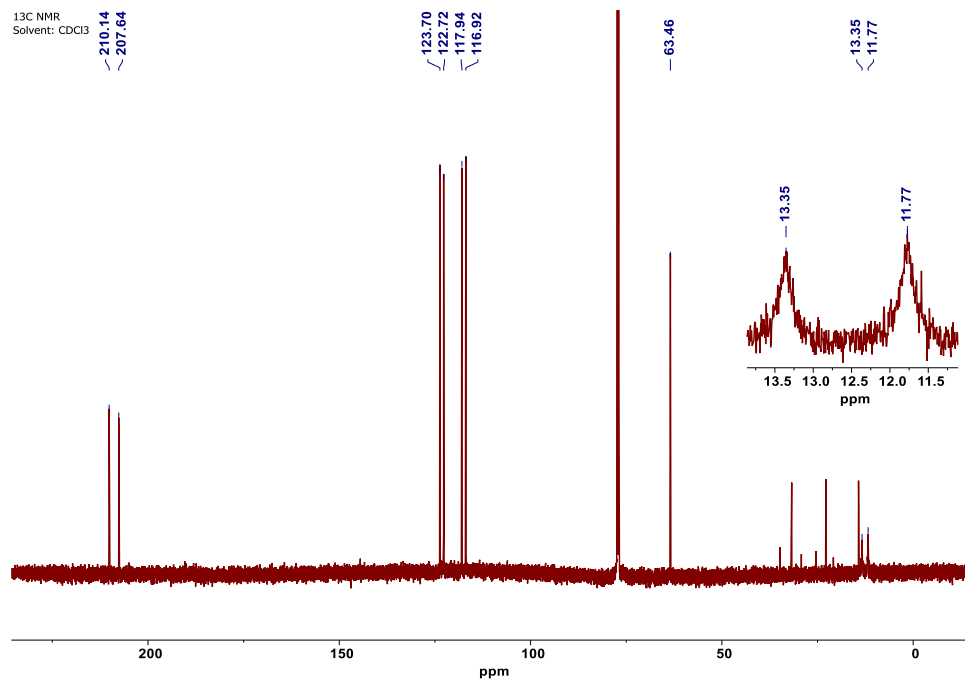
**Figure S6:** Isolation of oxidation (left) and reduction (right) waves of cyclic voltammogram of  $(^{\text{BMe}_2,\text{MeTC}^{\text{H}}})_2\text{U}$  (**1**). Waves are centered at 0.205 V and -2.46 V respectively. Both experiments are run at 100 mV/s.

<sup>1</sup>H NMR  
Solvent: CDCl<sub>3</sub>

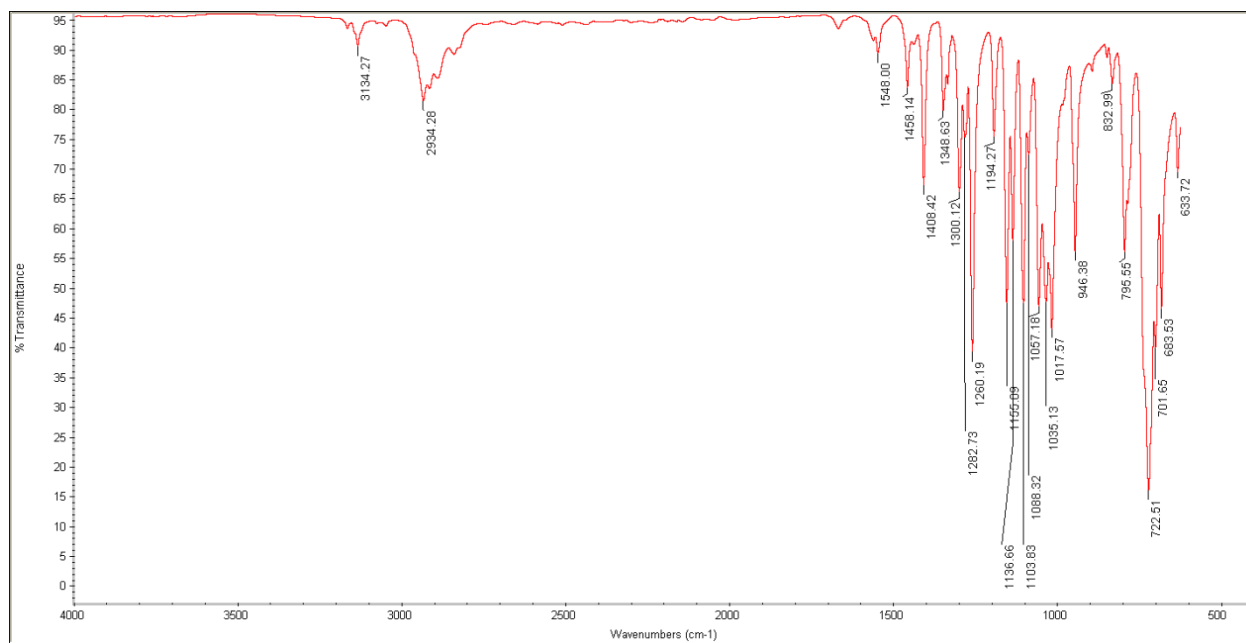


**Figure S7:** <sup>1</sup>H NMR of (BMe<sub>2</sub>,MeTCH)<sub>2</sub>Th (**2**) in CDCl<sub>3</sub>.

<sup>13</sup>C NMR  
Solvent: CDCl<sub>3</sub>

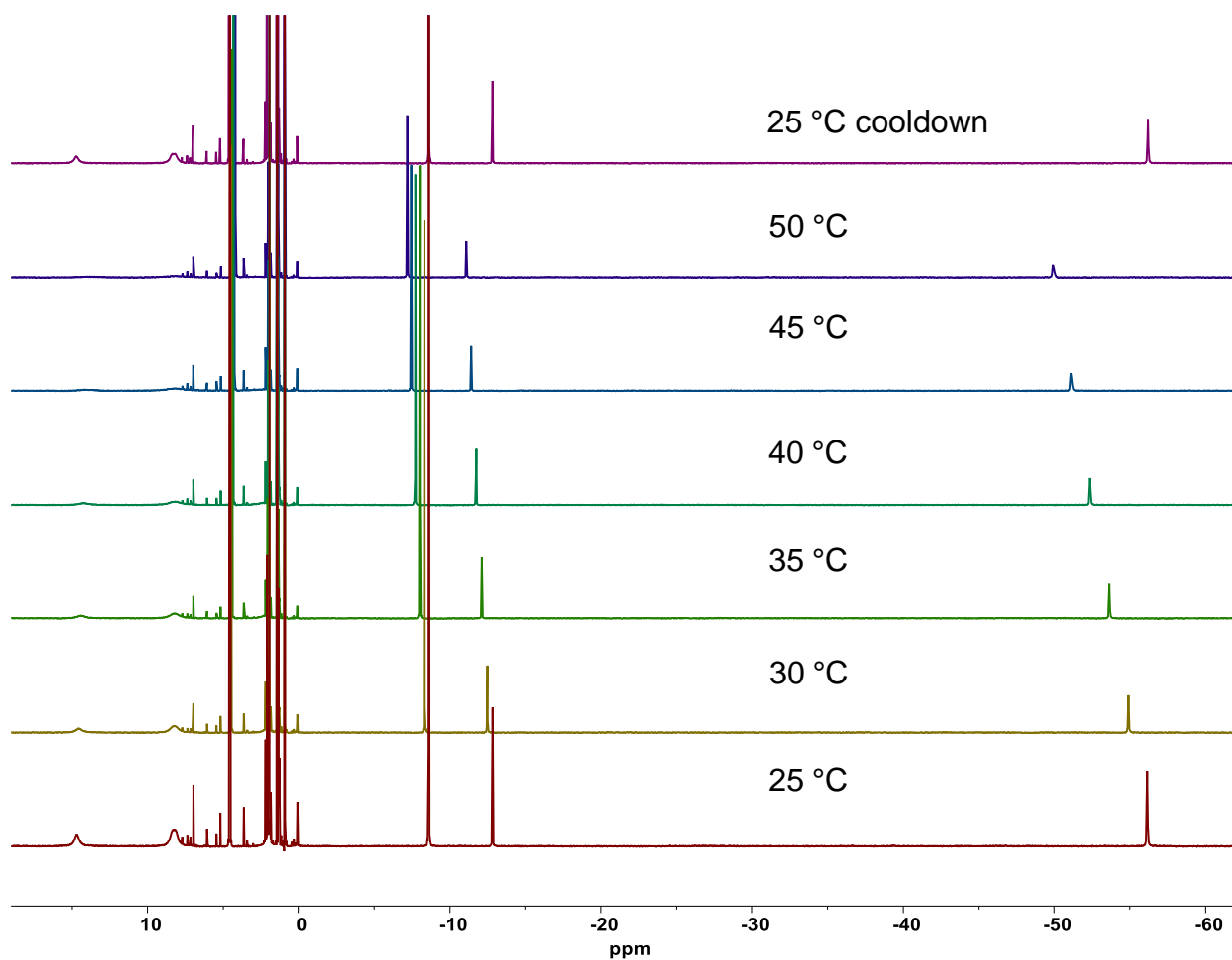


**Figure S8:** <sup>13</sup>C NMR of (BMe<sub>2</sub>,MeTCH)<sub>2</sub>Th (**2**) in CDCl<sub>3</sub>.

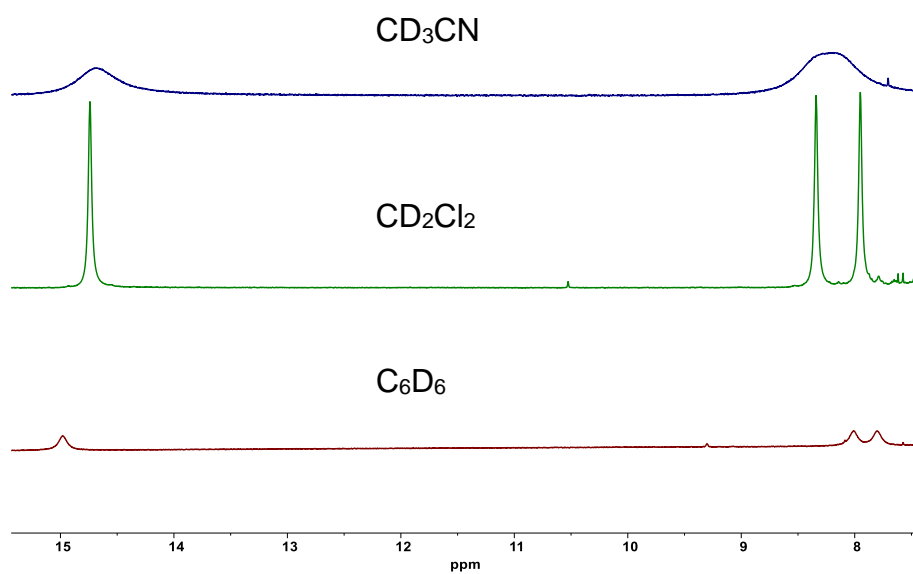


**Figure S9:** ATR IR of  $(\text{BMe}_2, \text{MeTC}^H)_2\text{Th}$  (**2**) drop cast as a solution in  $\text{CH}_2\text{Cl}_2$ .

**Additional NMRs for Reactions:**

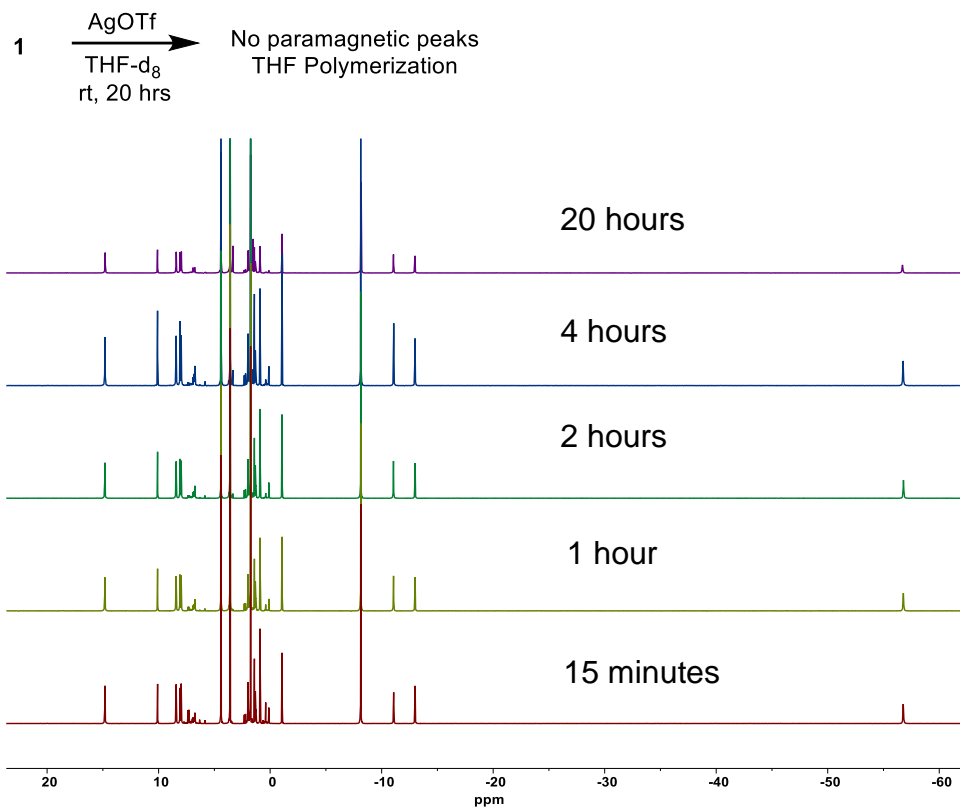


**Figure S10:** VT NMR of  $(^{BMe_2,Me}TC^H)_2U$  (1) in  $CD_3CN$ . The temperature was ramped from 25 °C (red) to 50 °C (blue) and back to 25 °C. The lowest frequency paramagnetic resonances are broadened nearly to baseline by 50 °C, and return to the original chemical shifts upon cooling.

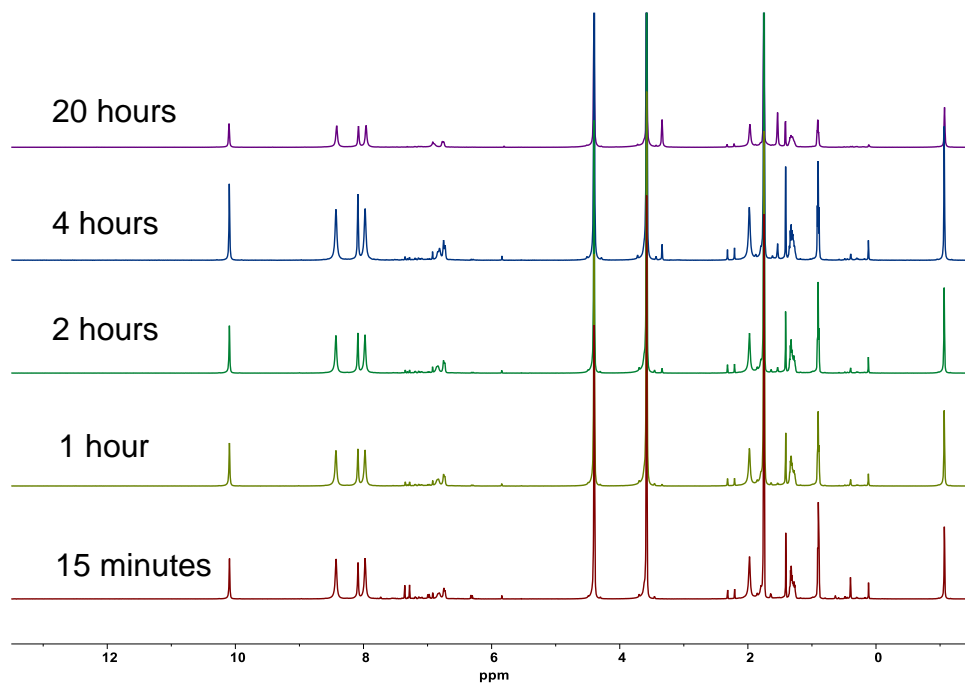
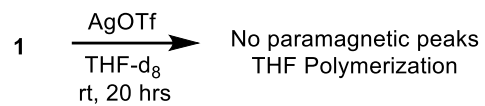


**Figure S11:** Comparison of upfield <sup>1</sup>H NMR signals of (BMe<sub>2</sub>,MeTC<sup>H</sup>)<sub>2</sub>U (**1**) in different solvents.

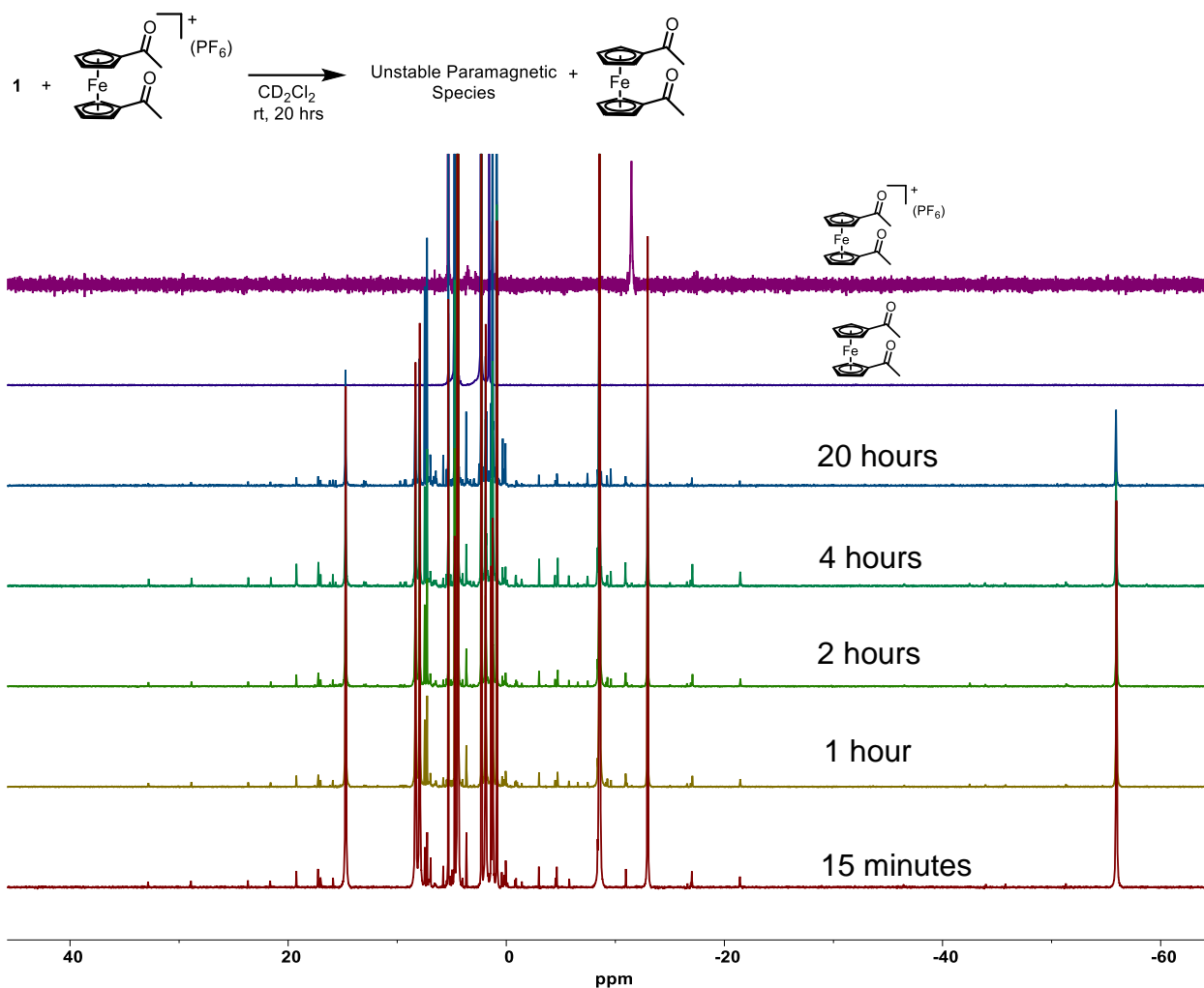




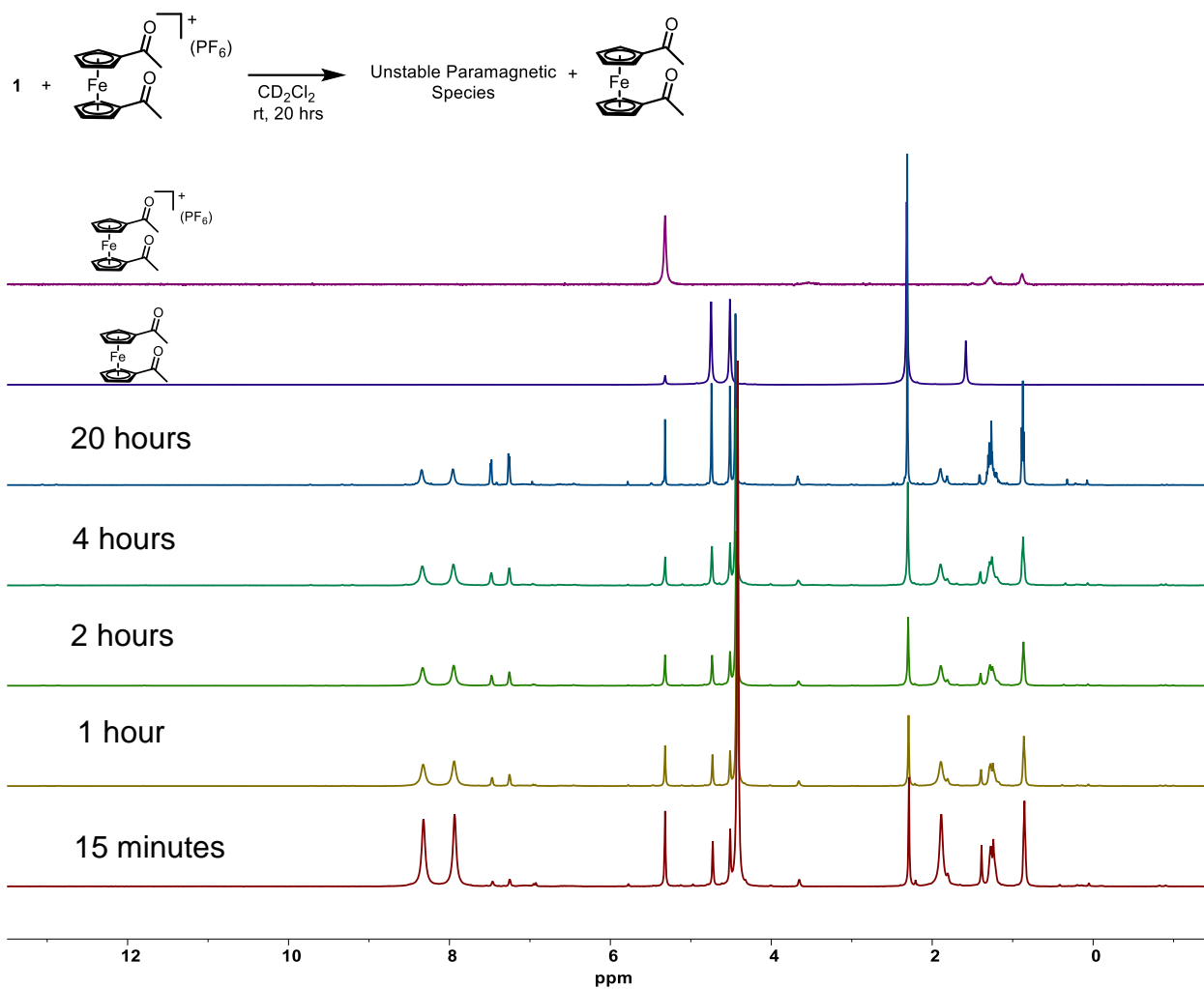
**Figure S12:** Reaction of  $(\text{BMe}_2, \text{Me}^-\text{TC}^H)_2\text{U}$  (**1**) with AgOTf in THF- $\text{d}_8$ . After 20 hours, the solution became a gel and no new paramagnetic signals appeared.



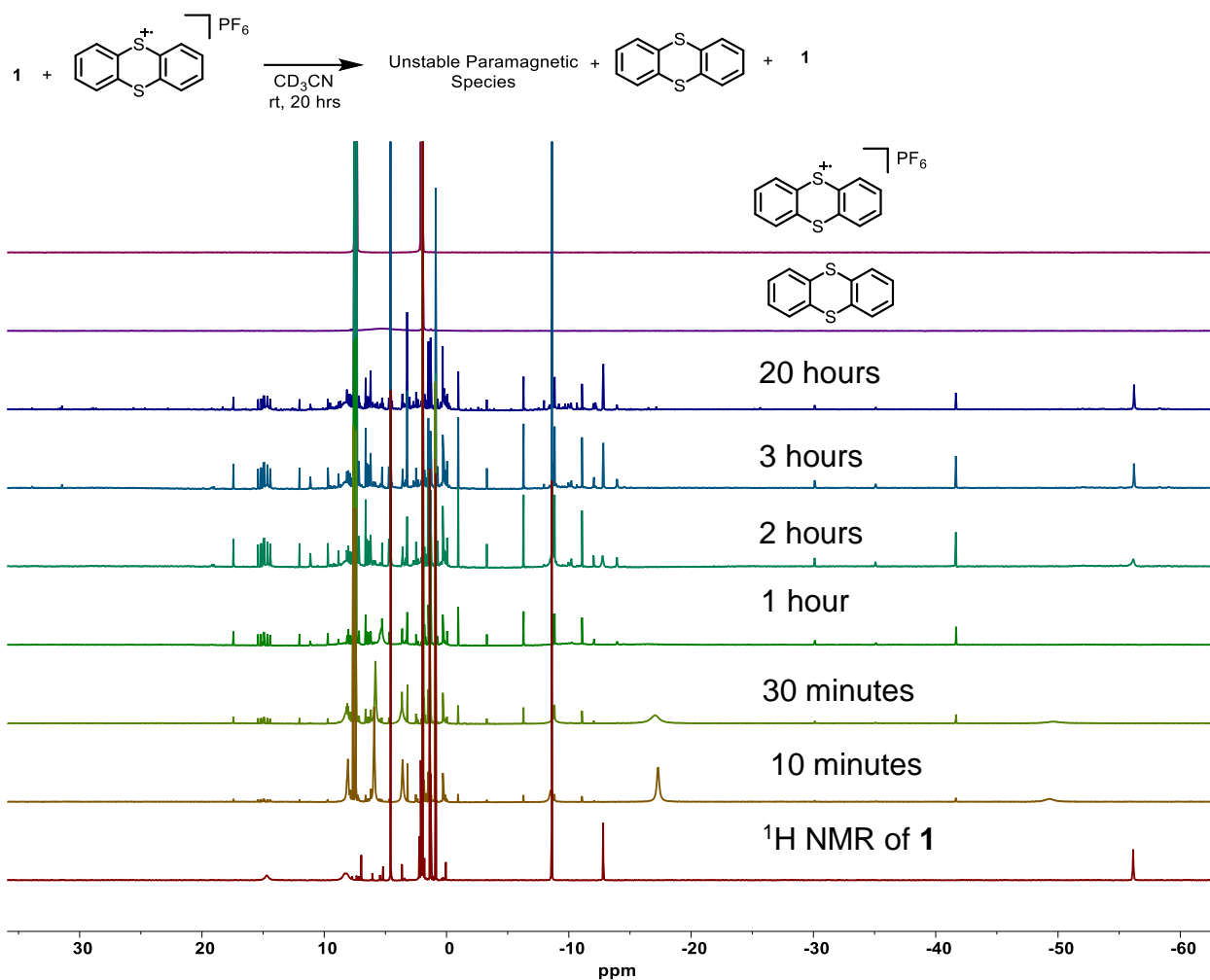
**Figure S13:** The diamagnetic region of the reaction solution of  $(^{\text{BMe}_2, \text{MeTC}^H})_2\text{U}$  (**1**) with AgOTf in THF- $\text{d}_8$  recorded regularly over a 20h reaction time period.



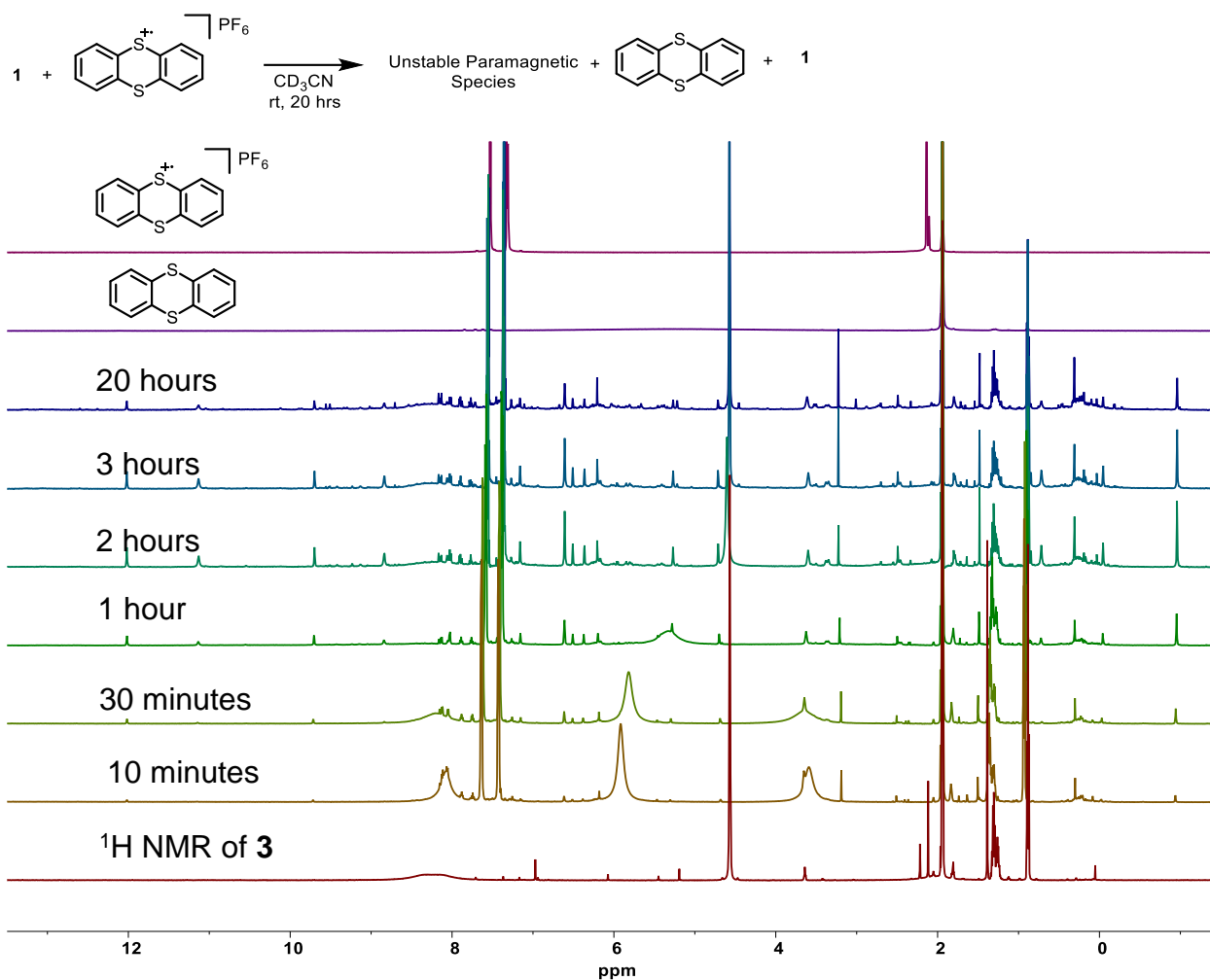
**Figure S14:** Reaction of  $(^{\text{BMe}_2, \text{MeTC}^{\text{H}}})_2\text{U}$  (**1**) with 1,1'-diacetylferrocenium- $\text{PF}_6$  in  $\text{CD}_2\text{Cl}_2$ . New paramagnetic peaks appear, but this new species appears not to be stable.



**Figure S15:** Close up of diamagnetic region for reaction of  $(^{\text{BMe}_2, \text{MeTC}^H})_2\text{U}$  (**1**) with 1,1'-diacetylferrocenium hexafluorophosphate. An increase of 1,1'-diacetylferrocene and consumption of **1** is observed over 20 h.



**Figure S16:** Reaction of  $(\text{BMe}_2, \text{MeTC}^H)_2\text{U}$  (**1**) with thianthrenium hexafluorophosphate in  $\text{CD}_3\text{CN}$ . Initially, **1** is quickly consumed and another set of paramagnetic resonances appear; these then disappear over the course of one hour as resonances for **1** reappear alongside a new, unidentified set of resonances.

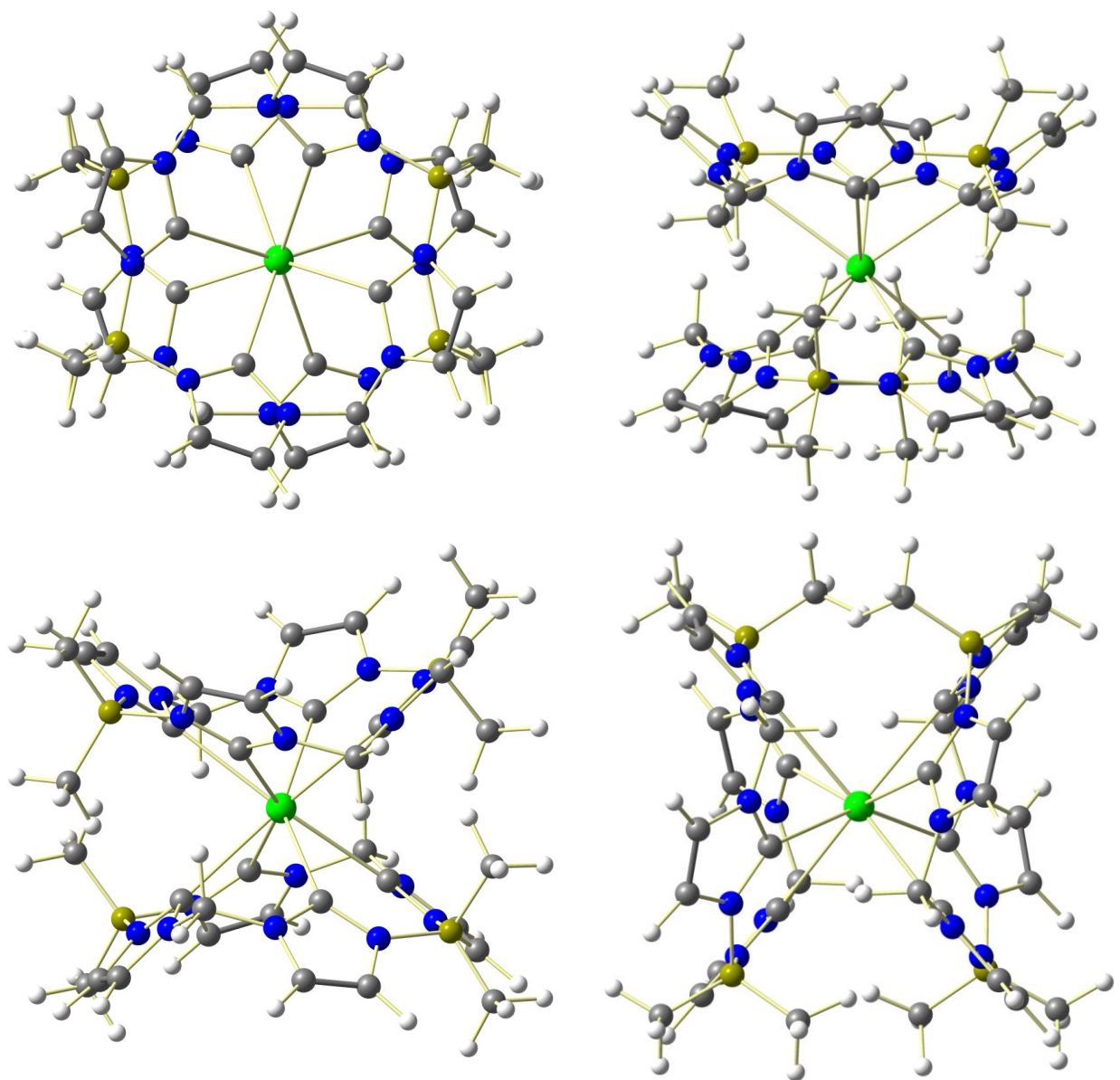


**Figure S17:** Close up of diamagnetic region for reaction of  $(^{\text{BMe}_2, \text{MeTC}^{\text{H}}})_2\text{U}$  (**1**) with thiathrenium hexafluorophosphate. Thiathrene formed is maximized after an hour.

## Computational Methods

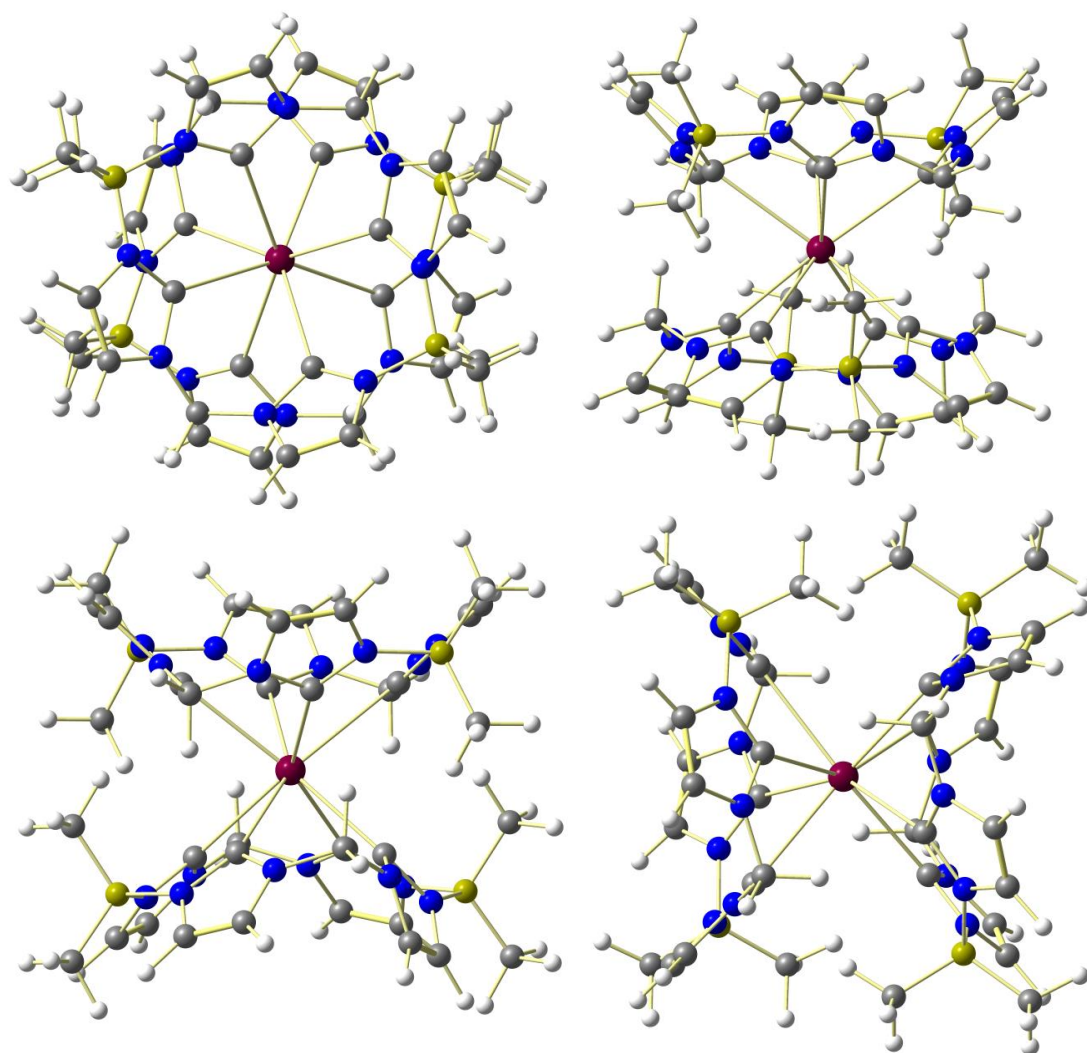
The compounds  $(^{\text{BMe}_2, \text{MeTC}^H})_2\text{U}$  (**1**),  $(^{\text{BMe}_2, \text{MeTC}^H})_2\text{Th}$  (**2**),  $(^{\text{BMe}_2, \text{EtTC}^H})_2\text{U}$  (**3**),  $(\text{COT})_2\text{U}$ , and  $(\text{COT})_2\text{Th}$  (COT = cyclooctatetraene) were optimized with the double- $\zeta$  correlation consistent basis set cc-pVDZ-PP,<sup>11, 12</sup> with the multielectron fit, fully relativistic ECP60MDF<sup>13, 14</sup> pseudopotential which includes 60 core electrons for uranium and thorium. The cc-pVDZ basis set was utilized for boron, nitrogen, carbon, and hydrogen atoms. Results are obtained with the exchange-correlation hybrid B3LYP energy functional.<sup>15</sup> The geometry optimizations are obtained without symmetry constraints to avoid pre-conceived assumptions. No complex modes were found through vibrational frequency calculations.

Geometry optimizations and harmonic vibrational frequency calculations were obtained with the NWChem 6.8 package.<sup>16</sup> The Natural Bond Orbital 7.0 (NBO7) program<sup>17</sup> was used to obtain NBO<sup>18</sup> population analysis. Basis sets and effective core potentials are obtained from the Environmental Molecular Sciences Laboratory (EMSL).<sup>19</sup> The ChemCraft package was utilized for computation visualizations.<sup>20</sup>

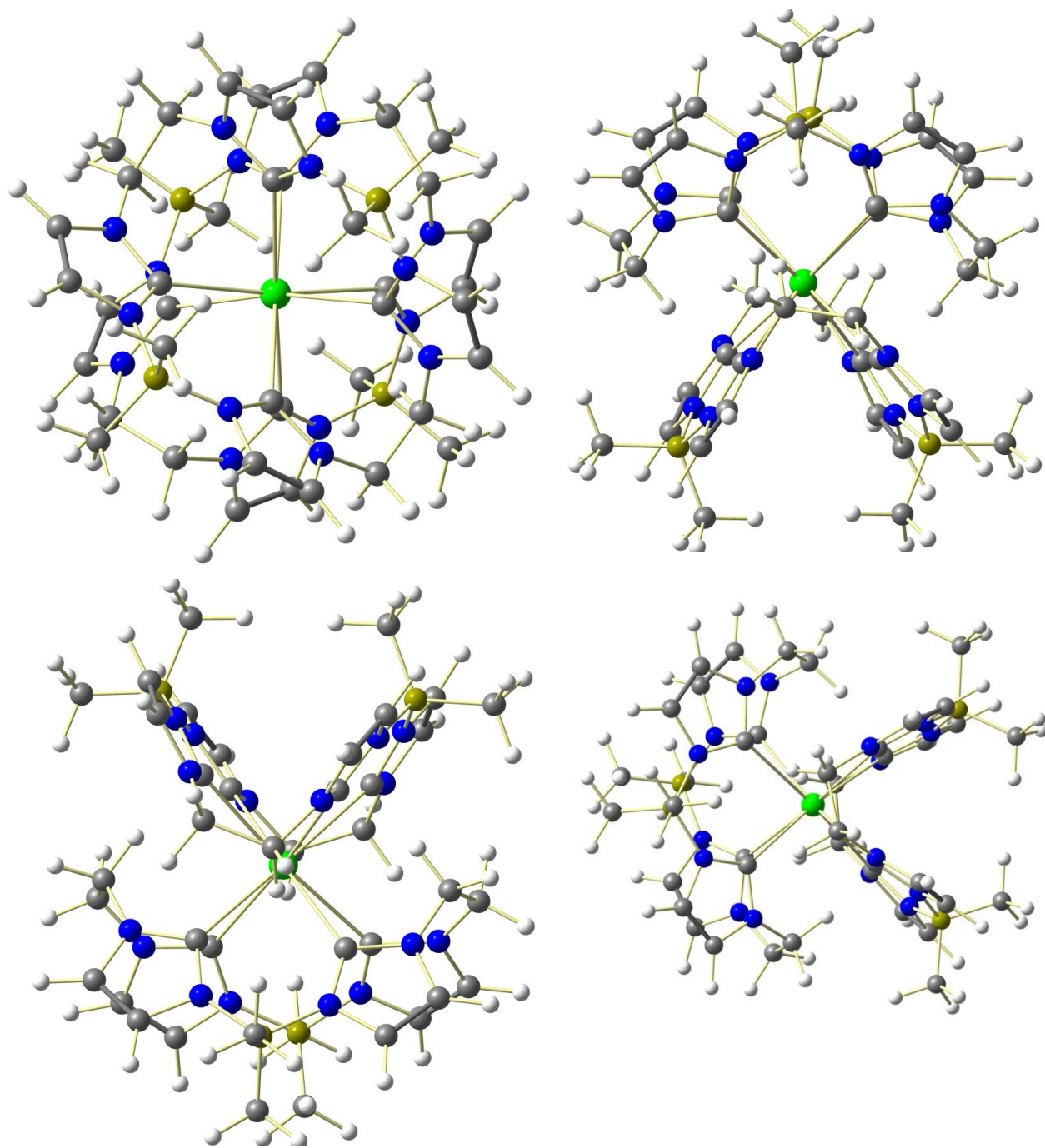


**Figure S18:** Optimized structure of  $(^{\text{BMe}_2.\text{MeTCH}})_2\text{U}$  (**1**). Green, blue, olive, gray, and white represent uranium, nitrogen, boron, carbon, and hydrogen, respectively.

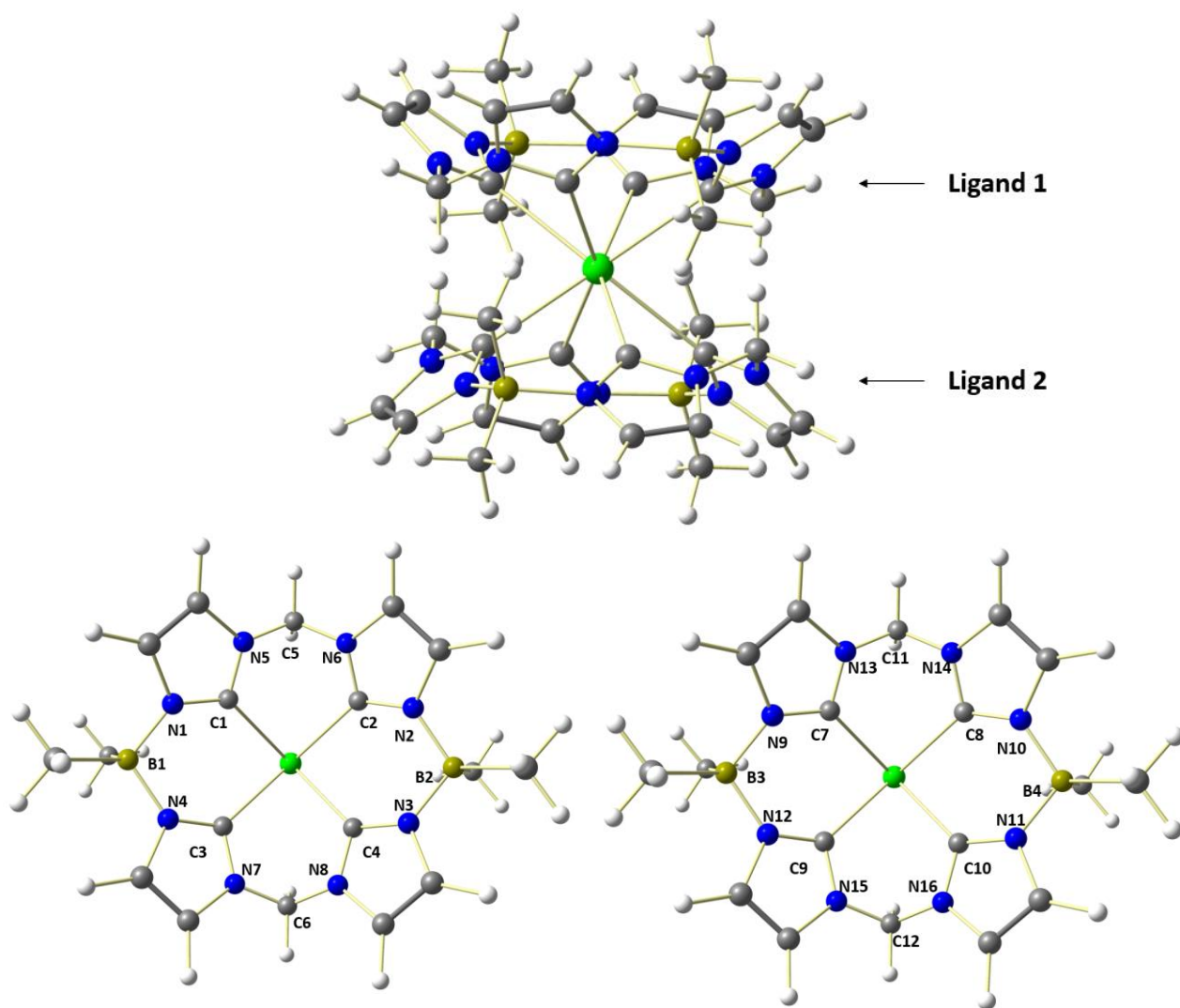




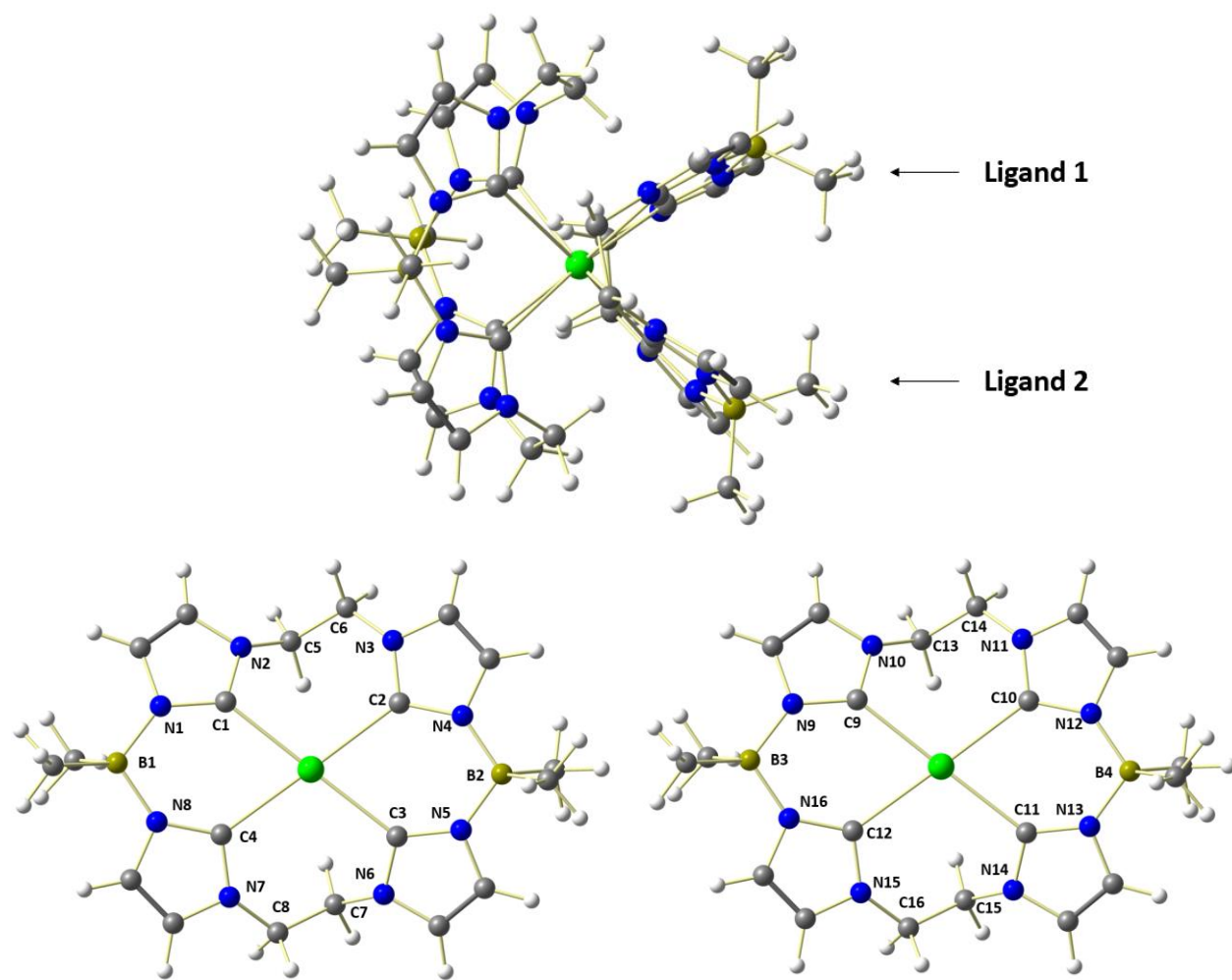
**Figure S19:** Optimized structure of  $(\text{BMe}_2, \text{MeTCH})_2\text{Th}$  (2).



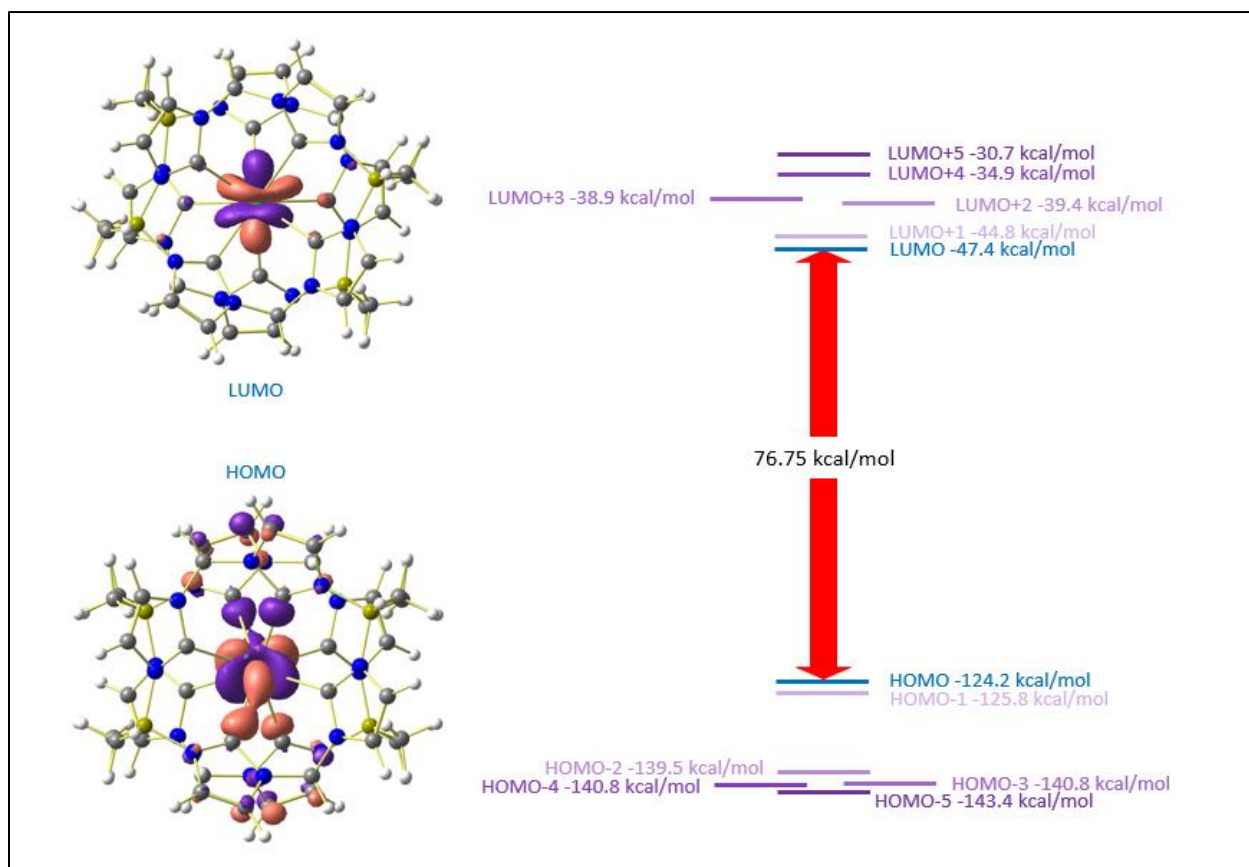
**Figure S20:** Optimized structure of  $(\text{BMe}_2, \text{EtTC}^H)_2\text{U}$  (**3**).



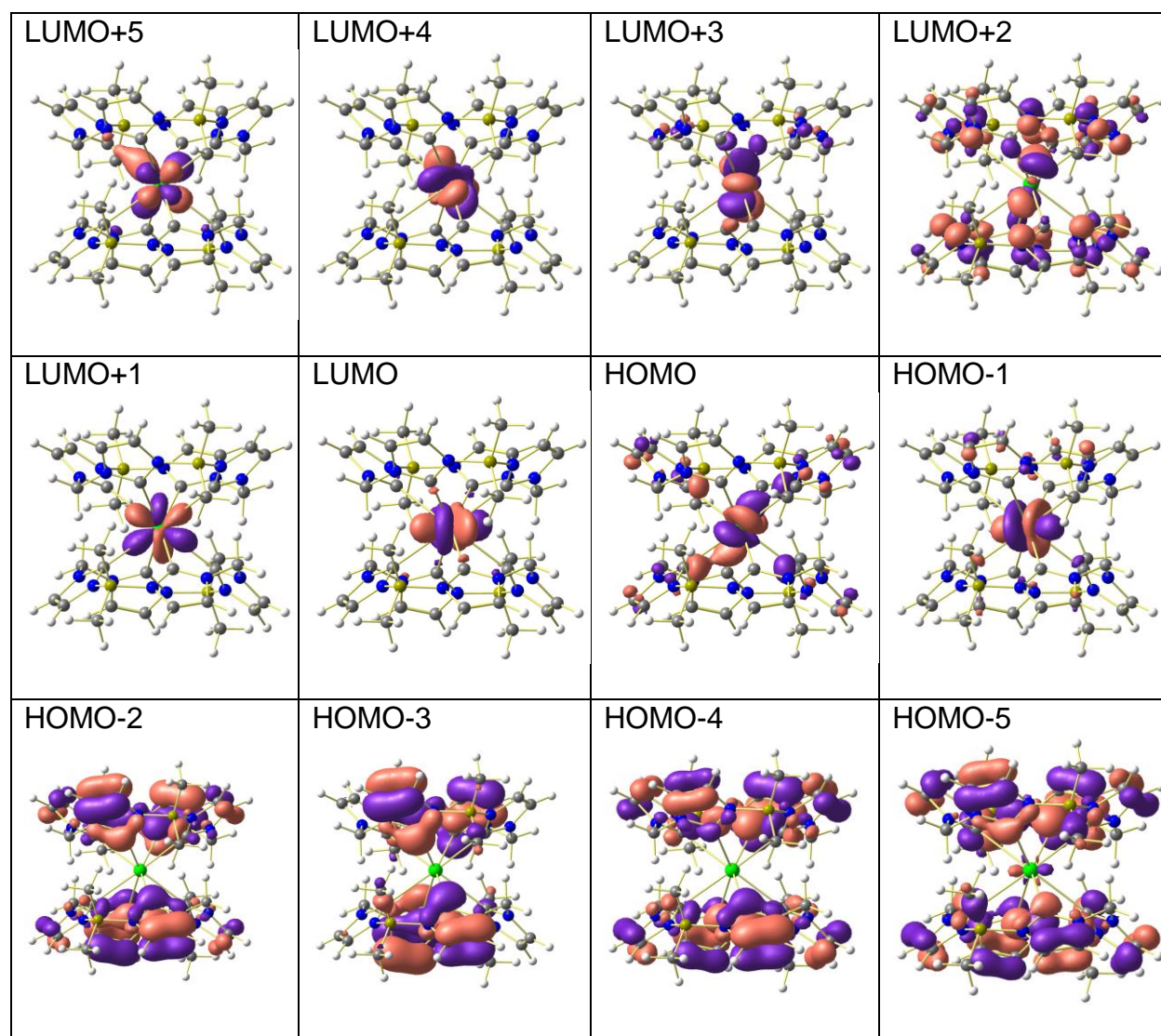
**Figure S21:** Labels for (BMe<sub>2</sub>,MeTC<sup>H</sup>)<sub>2</sub>U (1) and (BMe<sub>2</sub>,MeTC<sup>H</sup>)<sub>2</sub>Th (2).



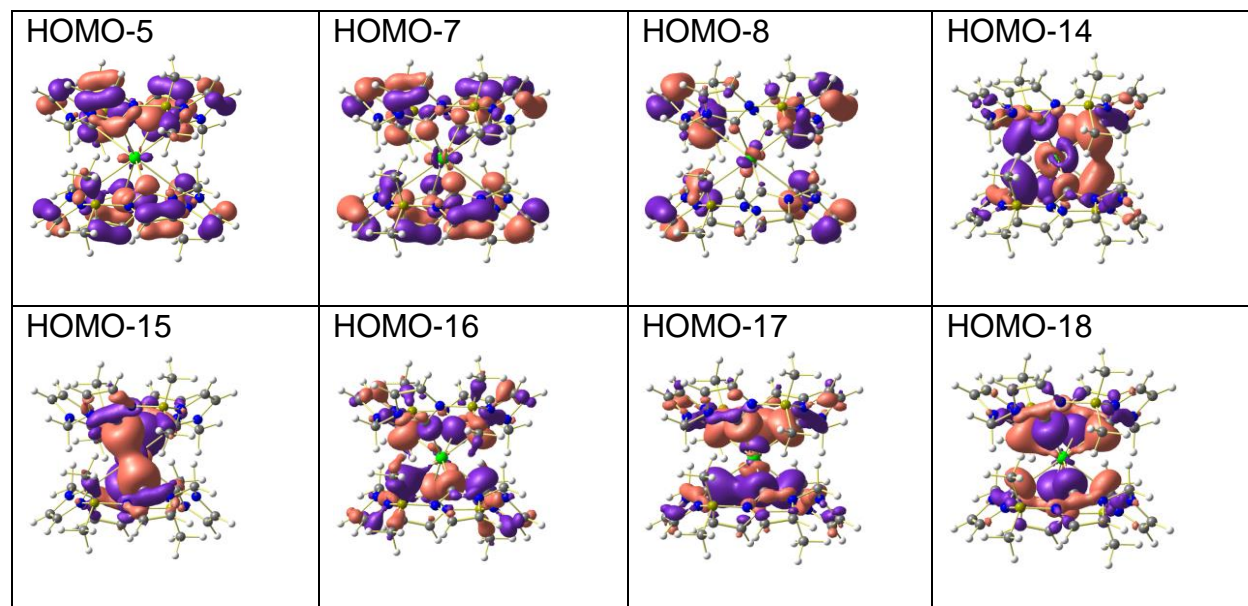
**Figure S22:** Labels for  $(\text{BMe}_2, \text{EtTC}^H)_2\text{U}$  (3).



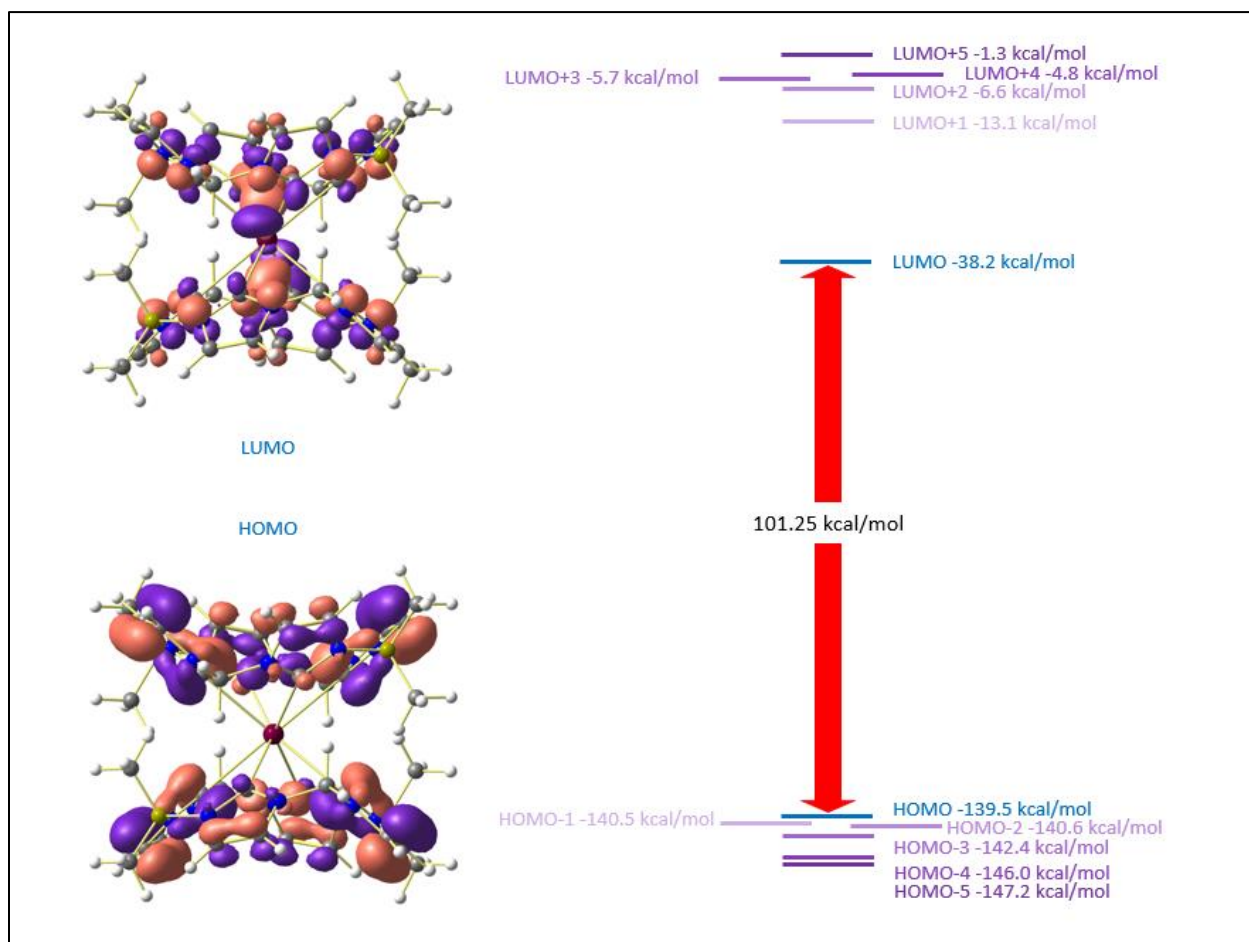
**Figure S23:** Right: MO diagram for  $(\text{BMe}_2.\text{MeTC}^H)_2\text{U}$  (1) showing orbital energies for HOMO to HOMO-5 and LUMO to LUMO+5. Left: Orbital diagrams built with canonical orbitals are shown for the HOMO and LUMO.



**Figure S24:** Orbital densities calculated for  $(^{\text{BMe}_2.\text{MeTC}^{\text{H}}})_2\text{U}$  (**1**) for LUMO+5 to HOMO-5 orbitals.

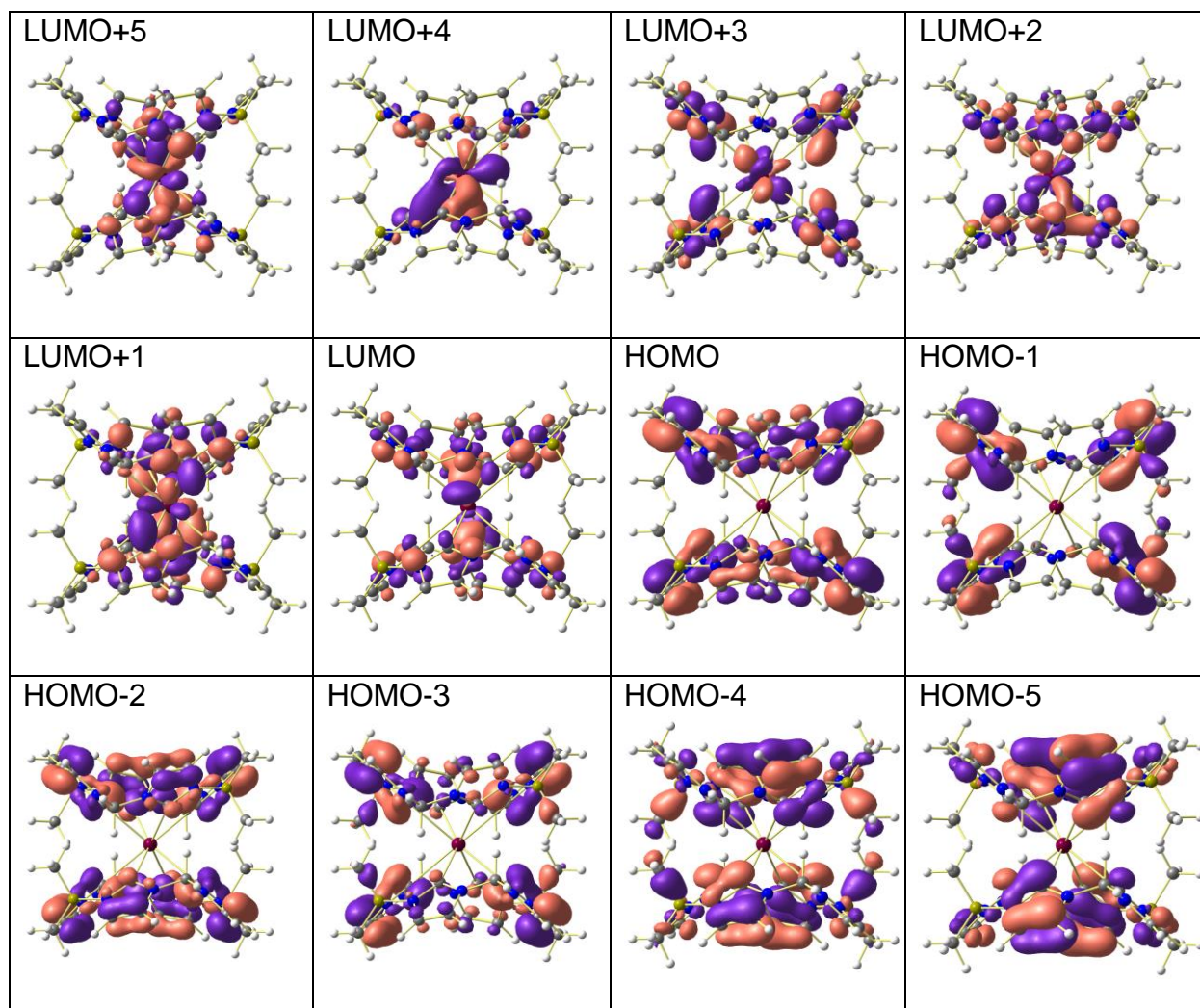


**Figure S25:** Orbital densities calculated for U-C orbitals in  $(^{\text{BMe}_2\text{MeTC}^{\text{H}}})_2\text{U}$  (**1**).

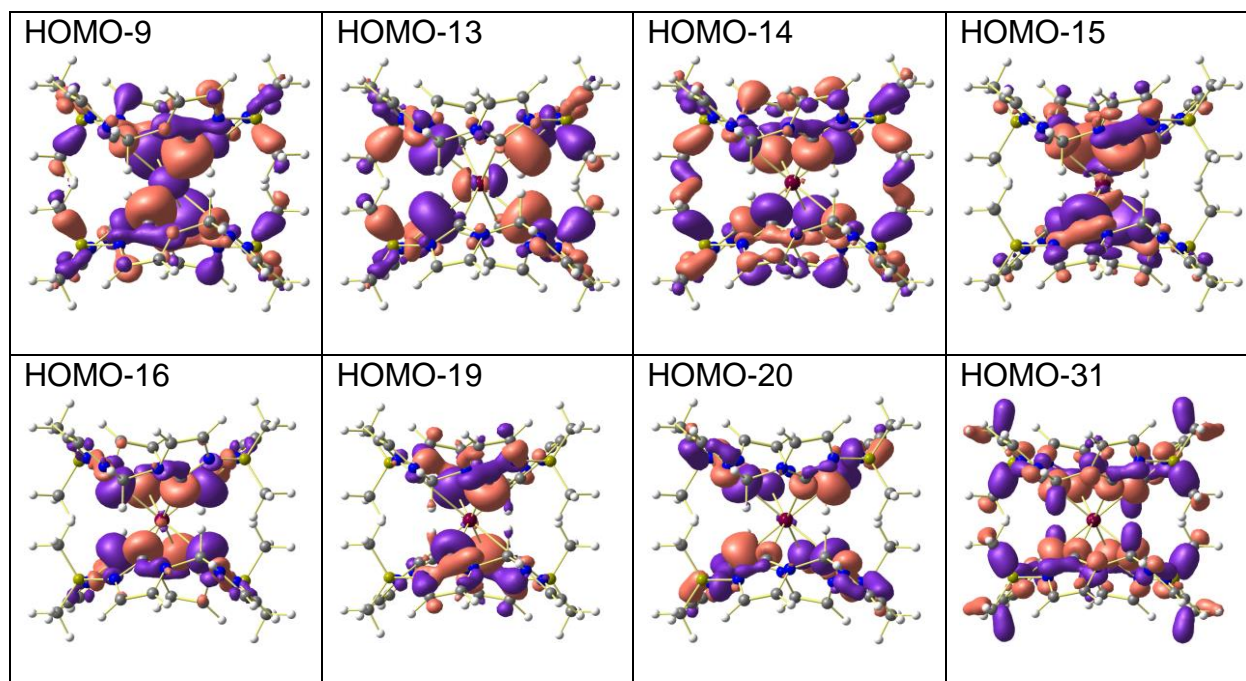


**Figure S26:** MO diagram for  $(^{\text{BMe}_2, \text{MeTC}^{\text{H}}})_2\text{Th}$  (2) showing orbital energies for HOMO to HOMO-5 and LUMO to LUMO+5. Orbital diagrams built with canonical orbitals are shown for the HOMO and LUMO.

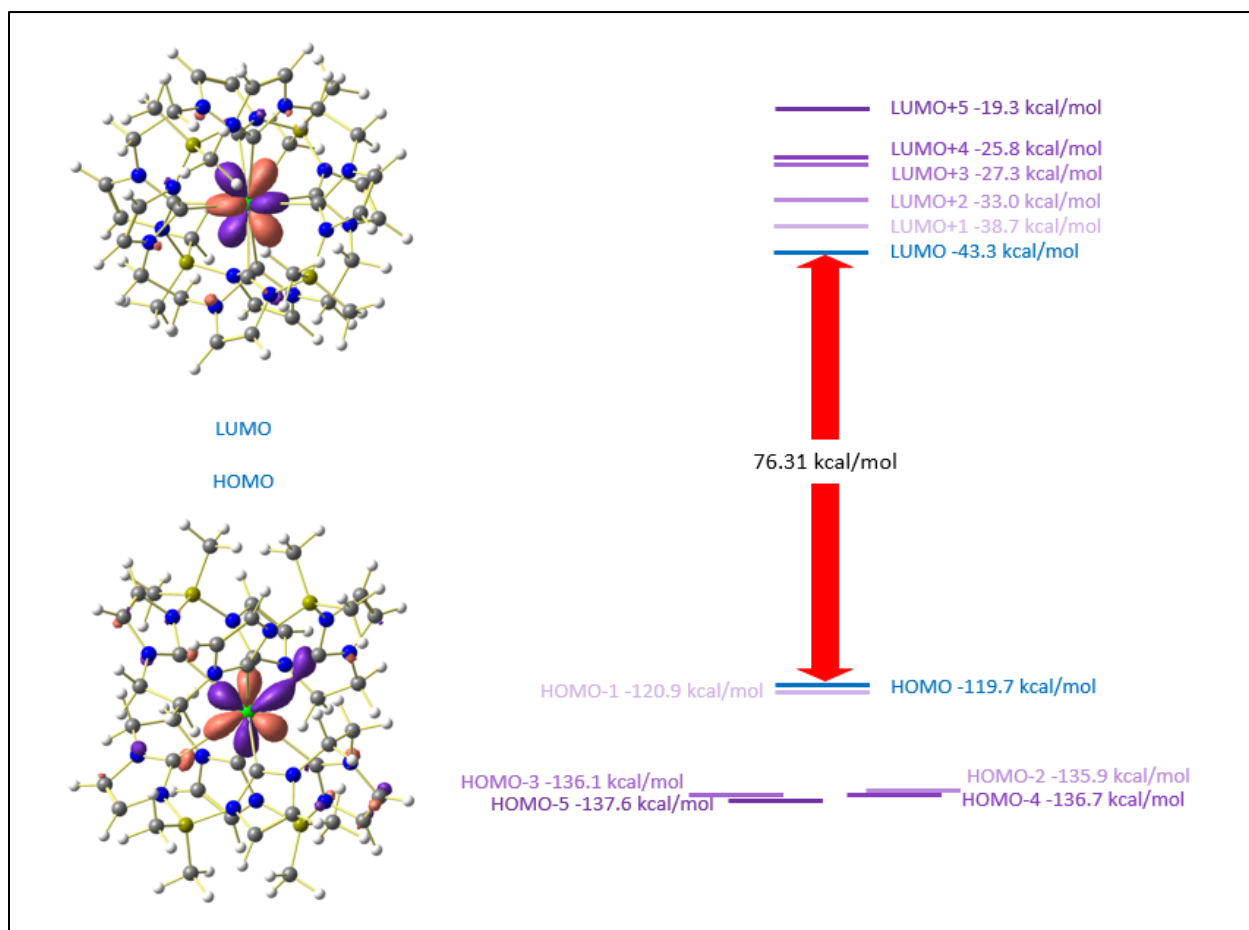




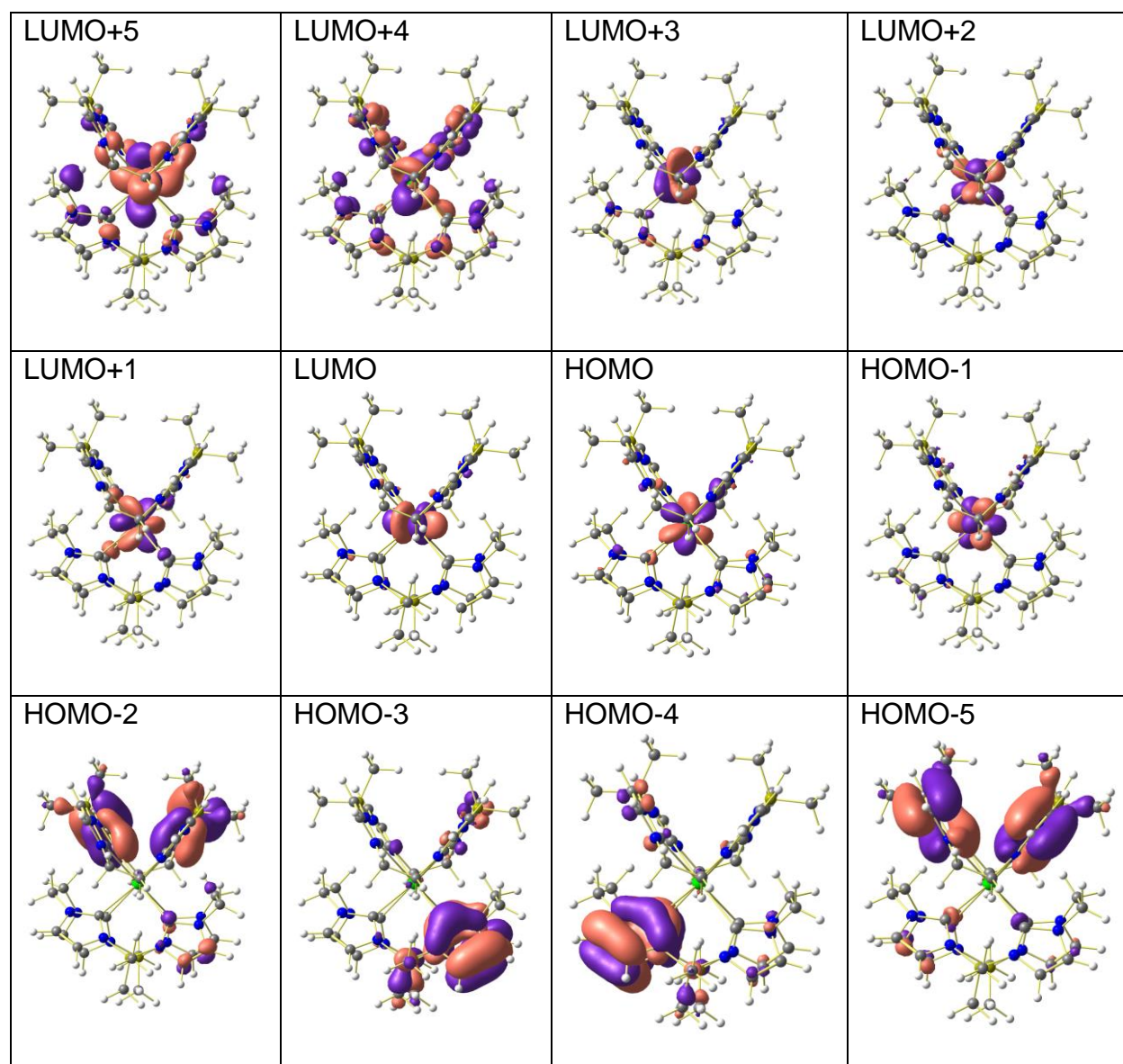
**Figure S27:** Orbital densities calculated for  $(^{BMe_2.Me}TC^H)_2Th$  (**2**) for LUMO+5 to HOMO-5 orbitals.



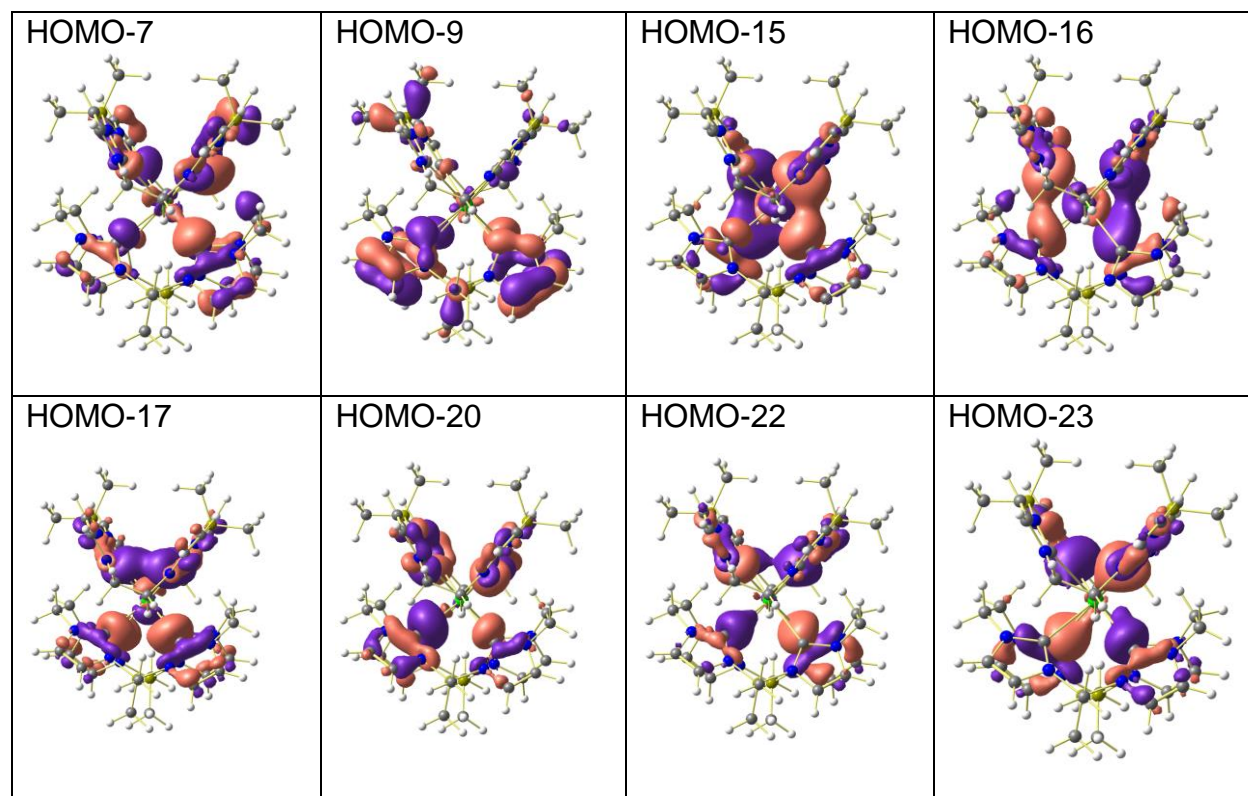
**Figure S28:** Orbital densities calculated for Th-C orbitals in  $({}^{\text{BMe}_2, \text{Me}}\text{TC}^{\text{H}})_2\text{Th}$  (**2**).



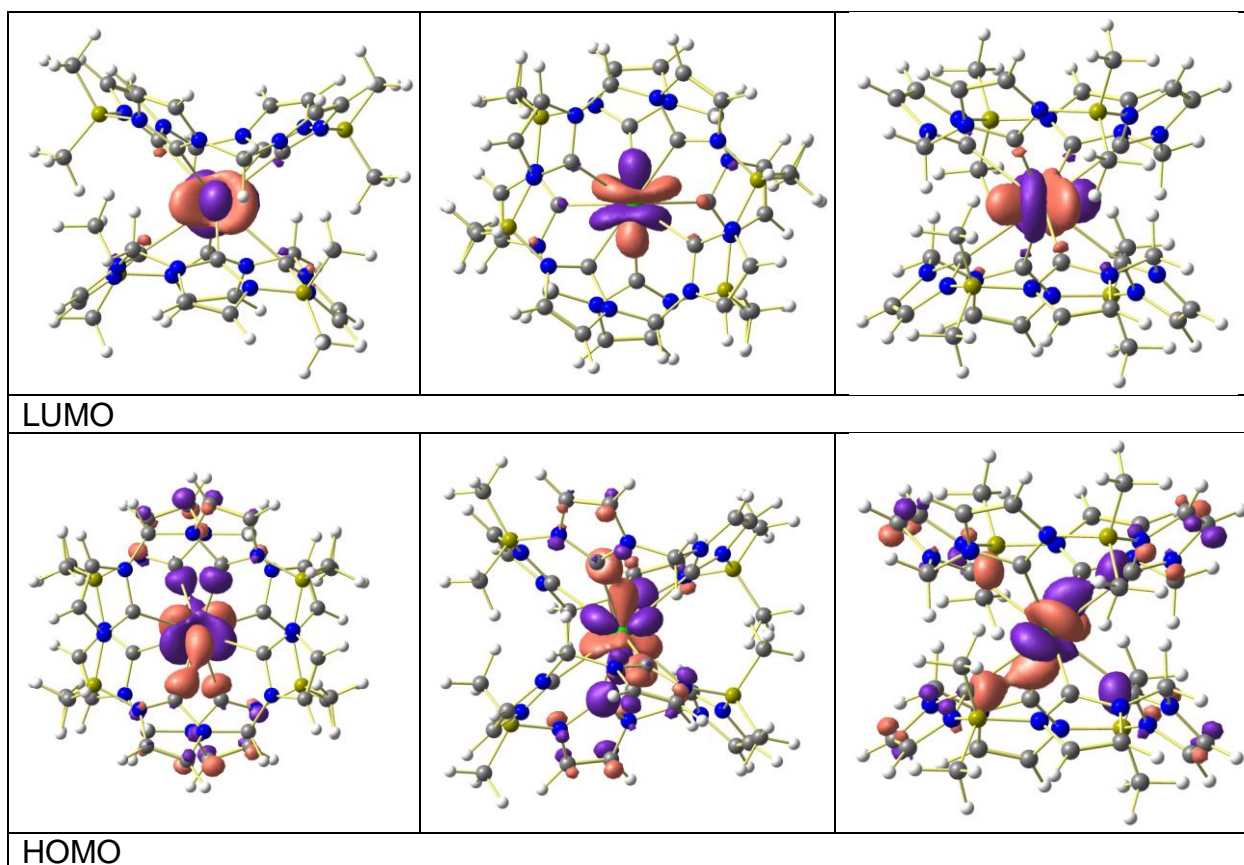
**Figure S29:** MO diagram for  $(^{\text{BMe}_2, \text{EtTC}^{\text{H}}})_2\text{U}$  (**3**) showing orbital energies for HOMO to HOMO-5 and LUMO to LUMO+5. Orbital diagrams built with canonical orbitals are shown for the HOMO and LUMO.



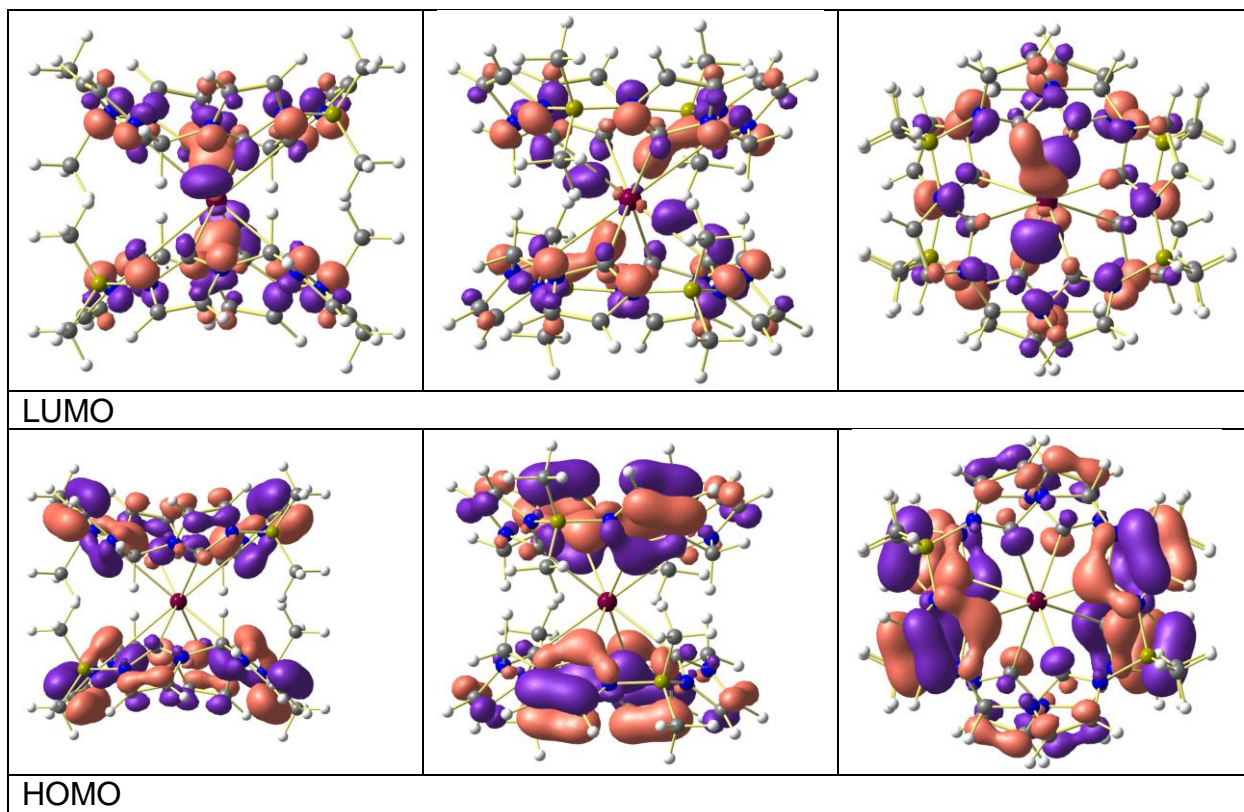
**Figure S30:** Orbital densities calculated for  $(^{\text{BMe}_2\text{EtTCH}})_2\text{U}$  (**3**) for LUMO+5 to HOMO-5 orbitals.



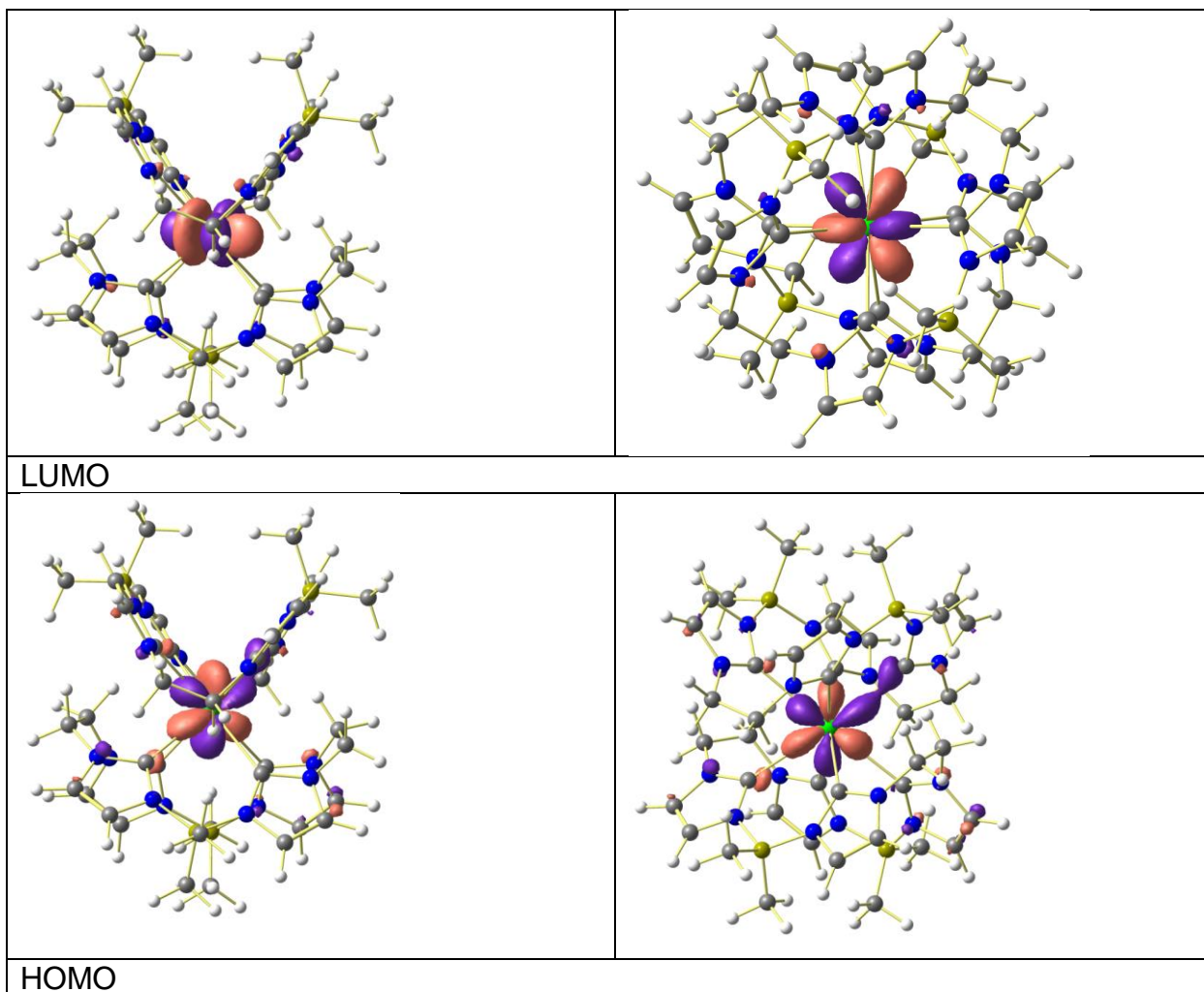
**Figure S31:** Orbital densities calculated for U-C orbitals in  $(^{BMe_2,Et}TC^H)_2U$  (**3**).



**Figure S32:** Additional views for HOMO and LUMO in  $(^{\text{BMe}_2.\text{MeTC}^H})_2\text{U}$  (**1**).



**Figure S33:** Additional views for HOMO and LUMO in  $(\text{BMe}_2\text{.MeTC}^H)_2\text{Th}$  (**2**).



**Figure S34:** Additional views for HOMO and LUMO in  $(^{\text{BMe}_2,\text{EtTC}^{\text{H}}})_2\text{U}$  (**3**).



**Table S3:** Differences between calculated and experimentally measured Th/U-C interatomic distances (in Å).

Label	$(^{\text{BMe}_2, \text{MeTC}^H})_2\text{M}$						$(^{\text{BMe}_2, \text{EtTC}^H})_2\text{U}$ (3)		
	$(^{\text{BMe}_2, \text{MeTC}^H})_2\text{Th}$ (2)			$(^{\text{BMe}_2, \text{MeTC}^H})_2\text{U}$ (1)			Comp	Exp	Diff
	Comp	Exp	Diff	Comp	Exp	Diff			
C1	2.77	2.69	0.07	2.70	2.62	0.08	2.66	2.62	0.04
C2	2.76	2.70	0.06	2.71	2.62	0.09	2.74	2.70	0.04
C3	2.76	2.70	0.06	2.71	2.62	0.09	2.75	2.62	0.14
C4	2.77	2.70	0.07	2.70	2.61	0.08	2.68	2.70	-0.02
C9	2.76	2.73	0.03	2.69	2.65	0.04	2.72	2.70	0.03
C10	2.77	2.70	0.06	2.71	2.63	0.07	2.64	2.62	0.02
C11	2.77	2.70	0.07	2.71	2.63	0.08	2.77	2.70	0.08
C12	2.76	2.72	0.04	2.69	2.65	0.05	2.67	2.62	0.05

**Table S4:** Calculated U/Th-B, U/Th-N, and U/Th-C interatomic distances in  $(\text{BMe}_2, \text{MeTC}^H)_2\text{U}$  (**1**),  $(\text{BMe}_2, \text{MeTC}^H)_2\text{Th}$  (**2**), and  $(\text{BMe}_2, \text{EtTC}^H)_2\text{U}$  (**3**).

	$(\text{BMe}_2, \text{MeTC}^H)_2\text{U}$ (1)	$(\text{BMe}_2, \text{MeTC}^H)_2\text{Th}$ (2)	$(\text{BMe}_2, \text{EtTC}^H)_2\text{U}$ (3)
B1	4.321	4.345	4.407
B2	4.323	4.345	4.384
N1	3.779	3.837	3.748
N2	3.791	3.834	3.530
N3	3.779	3.837	3.725
N4	3.790	3.833	3.763
N5	3.604	3.667	3.761
N6	3.616	3.660	3.725
N7	3.617	3.660	3.576
N8	3.604	3.667	3.754
<b>C1</b>	<b>2.697</b>	<b>2.767</b>	<b>2.659</b>
<b>C2</b>	<b>2.711</b>	<b>2.757</b>	<b>2.738</b>
<b>C3</b>	<b>2.712</b>	<b>2.757</b>	<b>2.751</b>
<b>C4</b>	<b>2.697</b>	<b>2.767</b>	<b>2.676</b>
C5	3.742	3.774	3.626
C6	3.742	3.774	4.071
C7	-	-	4.057
C8	-	-	3.700
B3	4.317	4.345	4.395
B4	4.319	4.345	4.411
N9	3.775	3.833	3.752
N10	3.785	3.837	3.693
N11	3.775	3.833	3.495
N12	3.784	3.837	3.747
N13	3.603	3.660	3.787
N14	3.614	3.667	3.752
N15	3.614	3.667	3.550
N16	3.602	3.660	3.760
<b>C9</b>	<b>2.694</b>	<b>2.757</b>	<b>2.724</b>
<b>C10</b>	<b>2.707</b>	<b>2.767</b>	<b>2.637</b>
<b>C11</b>	<b>2.707</b>	<b>2.767</b>	<b>2.773</b>
<b>C12</b>	<b>2.694</b>	<b>2.757</b>	<b>2.668</b>
C13	3.741	3.774	4.035
C14	3.741	3.774	3.563
C15	-	-	4.091
C16	-	-	3.641

**Table S5:** Orbital energies for HOMO/LUMO  $\pm 5$ , in kcal/mol. (HOMO/LUMO nomenclature is accurate for  $(^{\text{BMe}_2,\text{MeTC}^H})_2\text{Th}$  (**2**), as it is a closed-shell system which allows for doubly-occupied orbitals. U orbitals data in this table correspond to  $\alpha$  spin, and therefore to singly-occupied orbitals).

	$(^{\text{BMe}_2,\text{MeTC}^H})_2\text{U}$ (1)	$(^{\text{BMe}_2,\text{MeTC}^H})_2\text{Th}$ (2)	$(^{\text{BMe}_2,\text{EtTC}^H})_2\text{U}$ (3)
HOMO-5	-143.445	-147.208	-137.582
HOMO-4	-140.804	-146.034	-136.745
HOMO-3	-140.779	-142.422	-136.146
HOMO-2	-139.502	-140.578	-135.94
HOMO-1	-125.774	-140.451	-120.888
HOMO	-124.176	-139.469	-119.658
LUMO	-47.4212	-38.2165	-43.3437
LUMO+1	-44.8281	-13.1098	-38.7096
LUMO+2	-39.4437	-6.64007	-33.0499
LUMO+3	-38.9307	-5.70022	-27.3137
LUMO+4	-34.9218	-4.81462	-25.7945
LUMO+5	-30.7426	-1.27094	-19.3465

**Table S6:** (<sup>B</sup>Me<sub>2</sub>,MeTC<sup>H</sup>)<sub>2</sub>U (1) coordinates (in Å).

U	0.00139406	-0.00076434	-0.00124315
C	-1.63615508	0.72830864	-2.03510614
C	-1.665706	-2.03850414	-0.58777865
C	-1.47875773	-0.72859485	2.15098315
C	-1.61661306	2.03720723	0.70796632
C	-1.55480252	-1.55410106	-3.02913319
B	-2.27196158	-3.24816028	1.71944139
C	-1.32281158	1.55372619	3.13491094
B	-2.3951467	3.24864579	-1.54701267
N	-1.99086809	-0.17251115	-3.01405844
N	-2.0595619	-2.28085654	-1.88406258
N	-2.37252432	-2.9370548	0.15462315
N	-2.20425736	-1.83672644	2.47469197
N	-1.76115085	0.17290542	3.15237151
N	-1.91016939	2.28132302	2.03039909
N	-2.37509205	2.93781559	0.02093134
N	-2.38168421	1.83748833	-2.30554658
C	-3.17046257	1.61767196	-3.42498413
C	-2.93973333	0.35365839	-3.87114579
C	-2.98161648	-3.3070808	-1.95580129
C	-3.17032949	-3.71305211	-0.67171349
C	-2.64719101	-0.35157737	4.07531912
C	-2.91091175	-1.615512	3.64732245
C	-2.82048125	3.31076765	2.17137817
C	-3.10484512	3.71695705	0.90516627
H	-3.84103377	2.36974738	-3.8193527
H	-3.36149795	-0.20552365	-4.70044309
H	-3.41084662	-3.65246012	-2.89085641
H	-3.81397619	-4.49447504	-0.28984974
H	-3.55240907	-2.36694687	4.08858308
H	-3.00783672	0.20862665	4.93229322
H	-3.17605699	3.65803014	3.13617468
H	-3.77302541	4.50048917	0.57307609
H	-0.46056302	-1.59309977	-3.0232789
H	-0.23193313	1.59069987	3.0476298
C	-3.77001088	4.03885385	-1.92866869
H	-3.81878374	5.02037957	-1.42701894
H	-4.70181189	3.4963046	-1.68245551
H	-3.8047186	4.2812276	-3.00531646
C	-1.09933231	4.1391799	-1.94898371

H	-0.14665649	3.71425908	-1.6013598
H	-1.17138926	5.14954335	-1.50703294
H	-1.03004009	4.28040955	-3.04438416
C	-0.94616971	-4.13415459	2.02025293
H	-0.79383352	-4.27805603	3.1068568
H	-0.02457963	-3.70343202	1.60298708
H	-1.04692728	-5.14344221	1.58150981
C	-3.61070291	-4.04305603	2.20474106
H	-4.56079532	-3.50437278	2.03051658
H	-3.56208345	-4.28575879	3.28074542
H	-3.69320212	-5.02448325	1.70737331
H	-1.92819669	-2.03144834	-3.94238398
H	-1.62644684	2.03185458	4.07327654
C	1.62808969	0.71007216	2.04178265
C	1.47131776	-0.70779214	-2.16167164
C	1.67219379	-2.03607775	0.56980265
C	1.62020502	2.03769134	-0.69492982
C	1.55027938	-1.58033632	3.01561517
B	2.27561829	-3.22806685	-1.7477598
C	1.31598485	1.5823864	-3.12561585
B	2.39467994	3.23273306	1.57072072
N	1.98231588	-0.19777426	3.0144792
N	2.06025208	-2.29420985	1.86450667
N	2.37614255	-2.93035401	-0.18015403
N	2.20166477	-1.81108636	-2.49191907
N	1.75198141	0.20144296	-3.15663672
N	1.90742823	2.29829663	-2.01534576
N	2.37416534	2.93586614	-0.00013397
N	2.3765352	1.81598614	2.31857661
C	2.97608803	-3.32661143	1.92830299
C	3.16680843	-3.71981713	0.64059577
C	2.90955412	-1.57887825	-3.66187825
C	2.64202084	-0.31313311	-4.08145775
C	2.80965688	3.3360586	-2.14787939
C	3.09543355	3.73008182	-0.87820471
C	3.16670394	1.58674958	3.4353706
C	2.93413699	0.32040167	3.87330742
C	3.61736896	-4.01393138	-2.23974669
H	4.5653423	-3.47303333	-2.06095775
H	3.56976063	-4.24843192	-3.31759779
H	3.70367166	-4.9989774	-1.75030093
C	0.95324002	-4.11708119	-2.05515267
H	0.0298353	-3.69347333	-1.63452494

H	1.05808999	-5.12949622	-1.62463238
H	0.80143261	-4.25284706	-3.14288395
C	1.10135255	4.12390553	1.97978362
H	1.17550211	5.13738813	1.54537718
H	1.03315098	4.25694572	3.07627438
H	0.14732474	3.70382597	1.62980416
C	3.77189691	4.01605595	1.95850539
H	4.70199047	3.47244304	1.70827078
H	3.80730703	4.25083856	3.03680106
H	3.82380562	5.00095449	1.46391008
H	0.45614233	-1.62284916	3.00700658
H	1.92287466	-2.06559449	3.92501482
H	1.61853702	2.06901685	-4.05995518
H	0.22527437	1.62079726	-3.03592156
H	3.35548344	-0.24505843	4.69854585
H	3.83919866	2.33484728	3.8338873
H	3.40051644	-3.68408234	2.86099377
H	3.80809404	-4.50002564	0.25234086
H	3.55444372	-2.32485096	-4.10733743
H	3.00152315	0.25419224	-4.93421339
H	3.15973527	3.6962681	-3.10993046
H	3.75936239	4.5143849	-0.53951088

**Table S7:** (<sup>B</sup>Me<sub>2</sub>,MeTC<sup>H</sup>)<sub>2</sub>Th (**2**) coordinates (in Å).

Th	0.00633854	0.00138315	0.01351772
B	3.71378053	-1.02198712	-2.00838587
N	-1.48103378	-3.11145483	-1.22919761
C	-1.72698146	-1.75641282	-1.23712329
N	-2.7516901	-1.59848401	-2.12115536
B	-3.51214875	-0.2450349	-2.52465125
C	1.42272511	-2.06794673	-1.1316147
N	0.90520002	-3.34138059	-1.17577937
B	1.76730655	-2.36275323	3.20588799
C	1.86768223	0.89843235	-1.8273231
N	2.59246228	-2.14988327	-1.82473002
B	-1.94444074	3.6355177	1.38096472
C	-1.27340529	1.1521789	-2.14012536
N	1.65080157	2.05742674	-2.53888968
C	-2.1463491	0.97674685	1.43245018
C	-0.57936585	-1.68586499	2.12725415
N	2.95373759	0.32893448	-2.42114239
C	2.0219668	-0.05546386	1.89317901
N	-0.72701587	2.23106534	-2.79502494
N	-2.38436075	0.83961876	-2.86366747
C	0.46324567	2.54943287	0.99119843
N	-3.05941682	0.12492179	2.008809
C	-3.12059525	-2.82845404	-2.64387209
H	-3.92085106	-2.93689099	-3.36442349
C	-2.32100858	-3.78465887	-2.09779005
H	-2.27820529	-4.85895714	-2.24765903
N	-2.53597891	2.21854326	1.83437788
C	2.786867	-3.4466519	-2.27521151
H	3.65836787	-3.73837813	-2.84698199
N	-1.88346295	-1.9031723	2.51292981
C	1.72997276	-4.20402509	-1.87353202
H	1.50112469	-5.25512873	-2.01824115
N	0.16970203	-2.2538514	3.11353682
N	2.9054288	0.99135788	2.01607082
C	3.38782561	1.12012423	-3.47363791
H	4.24332573	0.85833262	-4.08270012
C	2.56920807	2.20354385	-3.56279909
H	2.56094161	3.04509761	-4.24845482
N	2.35184598	-0.90231996	2.90776843
C	-2.51591246	1.71361464	-3.93191916

H	-3.33443141	1.64970518	-4.63724089
N	1.73815364	2.96271541	1.30820511
C	-3.66604439	2.12584454	2.63231703
H	-4.14916341	2.99576522	3.05818491
C	-1.47712839	2.59213858	-3.89874662
H	-1.21553758	3.42260749	-4.54683756
N	-0.34724096	3.52860435	1.48188149
C	-4.0025959	0.81248627	2.749686
H	-4.81220182	0.32131597	3.28017926
C	-0.65799154	-2.80209471	4.08127652
H	-0.2721645	-3.30975188	4.95580223
C	-1.95028911	-2.57779928	3.71859896
H	-2.88825623	-2.83340301	4.201601
C	3.41765403	-0.38606149	3.6287745
H	3.84669462	-0.899827	4.47936806
C	3.77256047	0.80611872	3.07674221
H	4.54829593	1.51853856	3.33909435
C	0.41502837	4.51542361	2.08795583
H	-0.02610404	5.39310371	2.54230519
C	1.72633233	4.16404953	1.99367471
H	2.62960589	4.65258989	2.34558114
C	4.72949024	-1.45223951	-3.2071363
H	4.25048708	-1.62317784	-4.18940668
H	5.27910082	-2.37301228	-2.94636235
H	5.51603418	-0.69090526	-3.35241123
C	2.91428698	2.13430509	1.12577993
H	3.80782349	2.73588078	1.32950079
H	2.94833016	1.77889617	0.08905085
C	-3.02404821	-1.31348165	1.8390604
H	-3.94326226	-1.74248503	2.25473682
H	-2.97057034	-1.54530532	0.76869581
C	0.48295863	2.8979757	-2.35885923
H	0.38492923	3.15760123	-1.29807561
H	0.61246839	3.81617936	-2.94360513
C	-0.34861242	-3.71331751	-0.55231579
H	-0.45238112	-4.80409983	-0.58726246
H	-0.33778194	-3.3860884	0.49414352
C	4.52234776	-0.81910862	-0.61801116
H	5.10735042	-1.72309698	-0.36993628
H	3.8658575	-0.62538312	0.24295501
H	5.24491419	0.01576115	-0.69002083
C	-4.42292164	-0.51699481	-3.84764711
H	-4.97135991	0.39413484	-4.14253394



H	-5.21192947	-1.26099539	-3.63953079
H	-3.86593569	-0.86689582	-4.73694415
C	-4.42959199	0.28148592	-1.29620236
H	-5.01236949	1.17103876	-1.59625278
H	-3.84572012	0.57404804	-0.41118736
H	-5.16229681	-0.4859731	-0.98244591
C	2.33147804	-3.4148858	2.10917385
H	2.15931226	-3.09549392	1.07084716
H	1.87542473	-4.41475842	2.2379268
H	3.42272455	-3.54842196	2.22008174
C	2.18632762	-2.82128018	4.71186658
H	1.79768467	-3.82900898	4.94173611
H	1.84809244	-2.1452854	5.51942141
H	3.2817654	-2.9185507	4.80373102
C	-2.39924443	3.95941979	-0.14100478
H	-1.93201692	4.89138847	-0.51172221
H	-3.49250437	4.10876903	-0.19948161
H	-2.15532651	3.15369616	-0.84889526
C	-2.46836469	4.7959119	2.3973061
H	-2.07591585	5.78574531	2.10475167
H	-2.20922937	4.63970752	3.46124854
H	-3.56513053	4.90414702	2.34003889

**Table S8:** (<sup>BMe<sub>2</sub>,Et</sup>TC<sup>H</sup>)<sub>2</sub>U (**3**) coordinates (in Å).

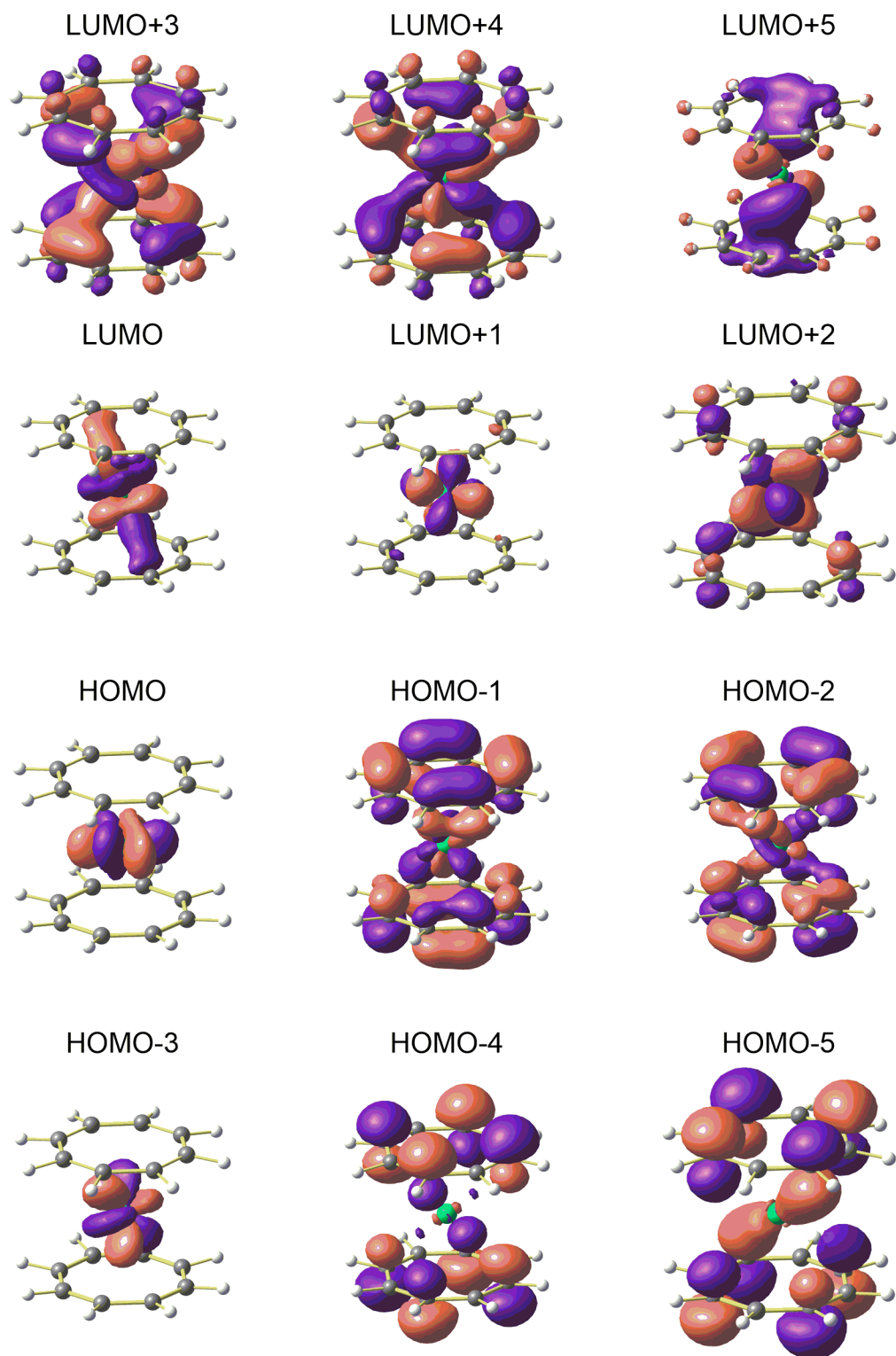
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C	-2.18839054	1.62600332	0.11438128
C	-0.09309492	1.57773822	2.14151696
C	2.21042721	1.51761933	0.11428445
C	0.28334911	1.80711683	-2.04926652
B	1.93327878	3.36763452	2.09683495
B	-1.78867922	3.57544259	-1.78031083
N	-3.23781021	1.5167491	1.01387813
N	-1.1529248	1.43941143	3.0100832
N	0.55145775	2.70447196	2.54158991
N	2.57287298	2.61247929	0.83901193
N	3.19730221	1.38321346	-0.84220212
N	1.35406915	1.86481806	-2.925292
N	-0.38680057	2.97839124	-2.25498835
N	-2.53534518	2.68312087	-0.6799678
C	-3.77197958	3.18725058	-0.29497083
C	-4.21074563	2.4695485	0.76550617
C	-1.18696914	2.47774875	3.92195625
C	-0.11674109	3.26372521	3.62477056
C	4.14597819	2.38170125	-0.72582507
C	3.75429638	3.14058566	0.33203609
C	1.35989116	3.05777824	-3.62700922
C	0.27330158	3.74687748	-3.20597801
H	-4.23026922	4.03468008	-0.78796349
H	-5.11342386	2.55147755	1.36201704
H	-1.94429888	2.56019765	4.69529895
H	0.22876338	4.16891709	4.11010851
H	4.22742426	4.01351923	0.76553301
H	5.00453751	2.45765642	-1.38577761
H	2.12430562	3.3021169	-4.35709095
H	-0.08523784	4.72089288	-3.51297467
C	-1.52239415	5.03511398	-1.10032725
H	-0.98456157	5.72940042	-1.76920704
H	-0.92763315	4.95461793	-0.17392333
H	-2.46460104	5.54481151	-0.83240672
C	-2.75090189	3.6587064	-3.10561932
H	-2.94058229	2.67431002	-3.57192723
H	-2.30873874	4.29498673	-3.8916433
H	-3.73903035	4.10054	-2.88824238
C	2.97777592	3.2377566	3.34953261

H	3.96228492	3.67968027	3.11301859
H	3.16462008	2.19268142	3.65867993
H	2.61312072	3.7712875	4.2454784
C	1.65655529	4.91511583	1.67094974
H	1.01081047	4.99686616	0.77981633
H	2.59079818	5.45890122	1.44371675
H	1.16762659	5.48862857	2.47838691
C	2.0767001	-1.84897636	-0.0697583
C	-2.16978272	-1.63332041	-0.02150506
C	0.19334161	-1.669426	2.07954396
C	-0.19168429	-1.41685308	-2.21016076
B	-1.77549052	-3.50860067	1.96210711
B	1.61256679	-3.42191922	-2.27271285
N	3.072242	-1.98338414	0.8860174
N	1.2262109	-1.51698698	2.97647279
N	-0.47287779	-2.77616587	2.49573429
N	-2.41833239	-2.77859472	0.68462392
N	-3.16842998	-1.59933903	-0.98457846
N	-1.22120343	-1.10986231	-3.07195789
N	0.4112033	-2.50293145	-2.75568821
N	2.21699559	-2.95388688	-0.86373443
C	1.22332863	-2.52742577	3.92022362
C	0.15103578	-3.30693901	3.61913459
C	-3.53182282	-3.42637498	0.16599359
C	-4.00155292	-2.69878329	-0.87538055
C	-1.26392119	-1.98999534	-4.13549078
C	-0.23250848	-2.85418263	-3.93680464
C	3.24866069	-3.75432382	-0.3895817
C	3.78626557	-3.15510504	0.69949316
C	-1.34014652	-5.01936802	1.52946497
H	-0.57843316	-5.01651936	0.73003899
H	-2.18716683	-5.62885037	1.16941939
H	-0.90930513	-5.57850022	2.37922082
C	-2.89458658	-3.48159142	3.1574416
H	-3.18086201	-2.45725637	3.46253206
H	-2.53864137	-3.99271639	4.06968088
H	-3.8274683	-3.99640377	2.86805208
C	2.80950379	-3.307232	-3.38358152
H	2.46687393	-3.60179833	-4.39182912
H	3.66384261	-3.96582634	-3.1475464
H	3.21737324	-2.28252627	-3.47555518
C	1.03328355	-4.93846556	-2.11240652
H	0.19648487	-4.98894973	-1.3935337

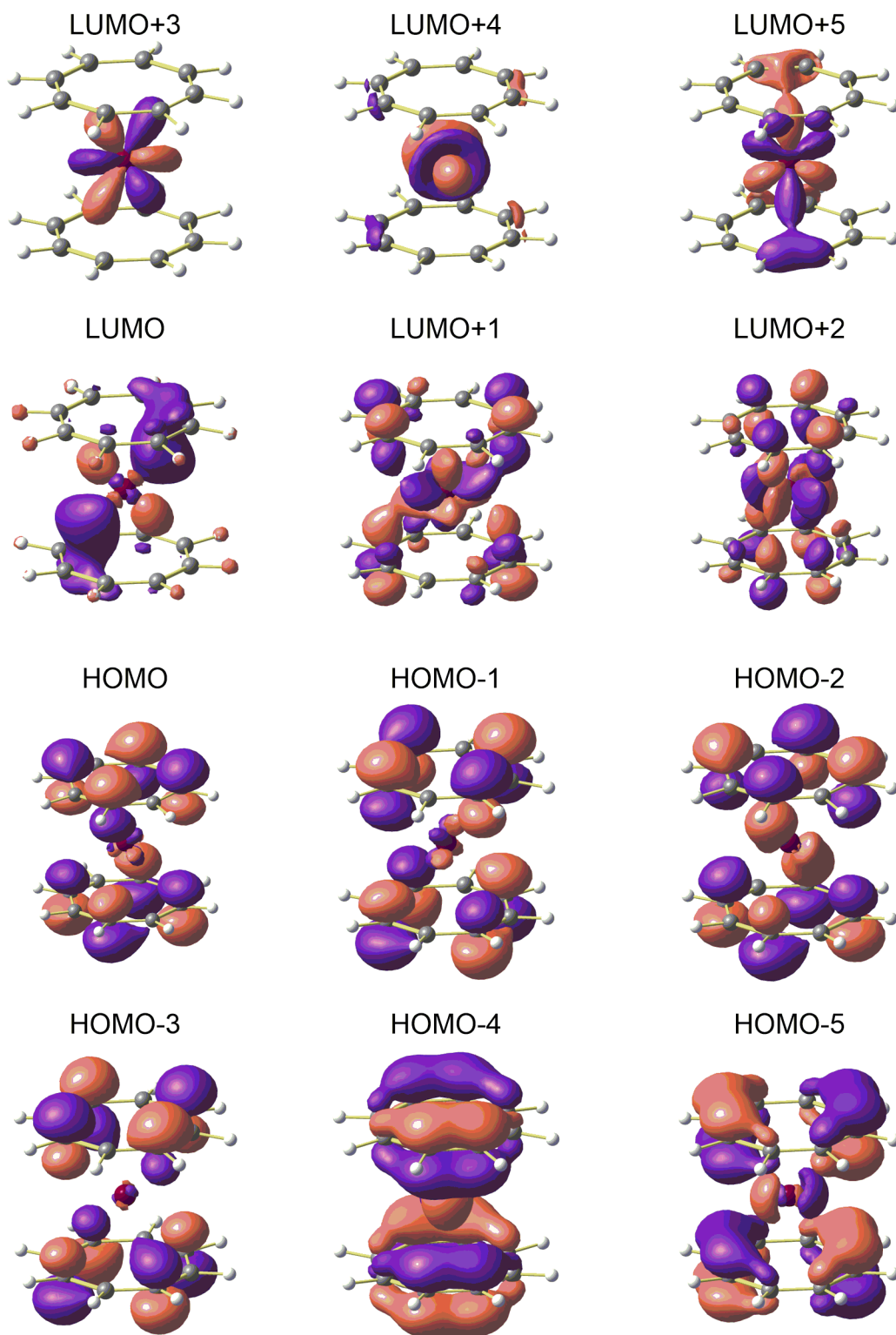
H	1.79718535	-5.65792442	-1.7700327
H	0.65773121	-5.33939482	-3.07057063
H	4.60008582	-3.45378319	1.35198486
H	3.52263425	-4.6864305	-0.86722319
H	1.9599212	-2.59398192	4.71481658
H	-0.22135309	-4.19164401	4.12146322
H	-3.89954306	-4.35916974	0.57407841
H	-4.84253115	-2.86346057	-1.54098241
H	-1.99946764	-1.91953876	-4.93078916
H	0.09418566	-3.68904988	-4.54499895
C	-2.2075821	-0.09398335	-2.78123398
C	-3.43482932	-0.59347521	-2.00926322
H	-2.55033516	0.36617535	-3.71960452
H	-1.70010775	0.69981845	-2.22584737
H	-3.93294001	0.28481612	-1.56925208
H	-4.14618734	-1.05860105	-2.70670094
C	3.45088564	-1.05946987	1.94986054
C	2.2802957	-0.54434675	2.79971443
H	3.98199839	-0.18882419	1.53391137
H	4.16205	-1.60641078	2.58500749
H	1.83431477	0.34238783	2.33953512
H	2.66192815	-0.22972664	3.78210265
C	-2.09896937	0.34422416	2.93395233
C	-3.38948294	0.62307413	2.15558287
H	-3.80136833	-0.34888178	1.84019126
H	-4.13174479	1.09867723	2.81281226
H	-2.36762928	0.02322203	3.95161192
H	-1.56800923	-0.49707695	2.47938312
C	2.38374375	0.86544247	-3.16921131
C	3.149217	0.40779815	-1.91162219
H	3.07650614	1.31578371	-3.89323556
H	1.94570924	-0.02586215	-3.64383773
H	2.67687709	-0.48948806	-1.4987903
H	4.17467466	0.12905982	-2.1953794

**Table S9:** Orbital energies for HOMO/LUMO  $\pm 5$ , in kcal/mol for (COT)<sub>2</sub>U and (COT)<sub>2</sub>Th. (HOMO/LUMO nomenclature is accurate for (COT)<sub>2</sub>Th, as it is a closed-shell system which allows for doubly-occupied orbitals. U orbitals data in this table correspond to  $\alpha$  spin, and therefore to singly-occupied orbitals).

	(COT) <sub>2</sub> U	(COT) <sub>2</sub> Th
HOMO-5	-137.8	-194.0
HOMO-4	-137.8	-194.0
HOMO-3	-125.7	-138.7
HOMO-2	-123.5	-138.7
HOMO-1	-123.5	-119.6
HOMO	-120.6	-119.5
LUMO	-32.2	-27.5
LUMO+1	-32.1	-18.5
LUMO+2	-32.0	-18.5
LUMO+3	-30.3	-8.5
LUMO+4	-30.3	-3.8
LUMO+5	-26.0	-3.8



**Figure S35:** Orbital densities calculated for  $(\text{COT})_2\text{U}$  for LUMO+5 to HOMO-5 orbitals.



**Figure S36:** Orbital densities calculated for  $(\text{COT})_2\text{Th}$  for LUMO+5 to HOMO-5 orbitals.

**Table S10:** (COT)<sub>2</sub>U coordinates (in Å).

U	-0.00002488	-0.00002072	0.00000497
C	-1.97823754	-1.77066212	-0.52855142
C	-1.97533994	-0.87726764	-1.62705159
C	-1.9887151	0.53028747	-1.7721554
C	-1.99175055	1.6268634	-0.8791323
C	-1.98875806	-0.53025918	1.77212571
C	-1.99182634	-1.62680174	0.8790988
H	-1.86659289	-2.81291489	-0.83949894
H	-1.86078179	-1.39406329	-2.58372752
H	-1.88317574	0.84245177	-2.81476991
H	-1.88854292	2.5848783	-1.39618671
H	-1.88321443	-0.84244801	2.81471203
H	-1.8886017	-2.58477777	1.39612076
C	-1.97532342	0.87729786	1.62705651
C	-1.9781694	1.77072459	0.52855116
H	-1.8607775	1.39407326	2.58376733
H	-1.86654905	2.81301725	0.83952807
C	1.97473302	0.83955683	1.64665111
C	1.98745383	-0.57111898	1.7593848
C	1.99238894	-1.64680629	0.84136153
C	1.98742015	0.57109894	-1.75940842
C	1.99233624	1.64682006	-0.84138531
C	1.97956021	1.75812676	0.56913571
H	1.86008162	1.33419978	2.61496764
H	1.88116233	-0.90719982	2.79443846
H	1.8896163	-2.61655547	1.33601696
H	1.88105787	0.90717493	-2.79448132
H	1.88943134	2.61660353	-1.33606301
H	1.86874526	2.79304142	0.90417749
C	1.97959989	-1.75811234	-0.56912579
C	1.97473687	-0.83957341	-1.64664038
H	1.8601221	-1.33422007	-2.61493527
H	1.86890584	-2.79299034	-0.90414865



**Table S11:** (COT)<sub>2</sub>Th coordinates (in Å).

Th	-0.00000941	-0.00011089	-0.00001986
C	-2.04260768	-1.68446014	-0.76699718
C	-2.04270491	-0.64865632	-1.73362915
C	-2.04228612	0.76728531	-1.68460539
C	-2.04230174	1.73392996	-0.64880913
C	-2.04246613	-0.76683539	1.68473751
C	-2.04277044	-1.73347566	0.64894154
H	-1.95086004	-2.67629052	-1.21854161
H	-1.95085706	-1.03075532	-2.75422737
H	-1.95037759	1.21880938	-2.67642818
H	-1.9501952	2.75450224	-1.0309103
H	-1.95067897	-1.2183871	2.67656027
H	-1.95095991	-2.7540787	1.03103774
C	-2.04241312	0.64910279	1.73376195
C	-2.04204686	1.68491023	0.76713021
H	-1.95042735	1.03117666	2.75435575
H	-1.94999199	2.67671232	1.21866739
C	2.04251578	0.61122302	1.74732666
C	2.04249491	-0.80332868	1.66770848
C	2.0425395	-1.74731988	0.61124569
C	2.04239809	0.80333635	-1.66767047
C	2.04240917	1.74733151	-0.61120782
C	2.04235389	1.66769826	0.8033449
H	1.95061604	0.97112024	2.77594862
H	1.95066649	-1.27623017	2.64953737
H	1.95061636	-2.77594028	0.97114618
H	1.95048349	1.27622996	-2.64949389
H	1.95037018	2.77593939	-0.97110705
H	1.95041944	2.64950969	1.27625763
C	2.04252572	-1.66769097	-0.80330531
C	2.04257302	-0.61121922	-1.74728804
H	1.95068335	-0.97112415	-2.77590944
H	1.95068512	-2.64951206	-1.27622266

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